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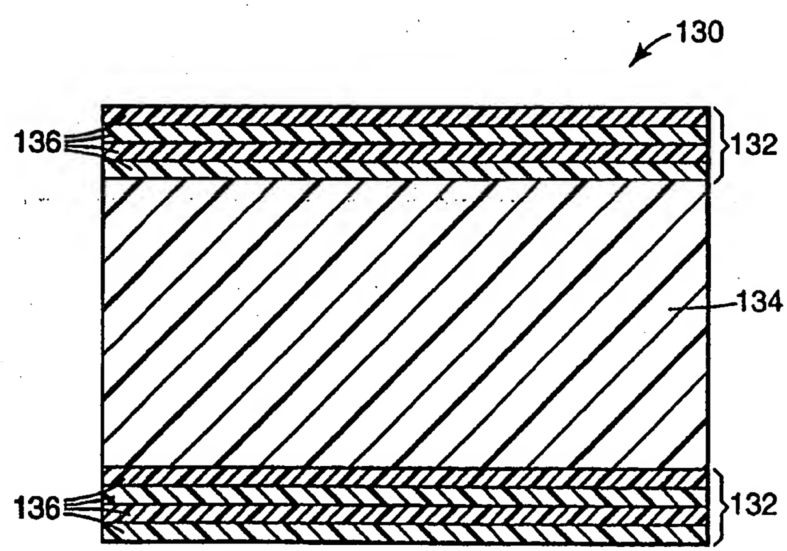

(57) Abstract

Various anti-reflective polymer constructions, articles incorporating such constructions, and processes for preparing such constructions are described.

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ANTI-REFLECTIVE POLYMER CONSTRUCTIONS AND METHOD FOR PRODUCING SAME

Background of the Invention

This invention relates to providing anti-reflective properties.

Anti-reflective layers, e.g., in the form of thin films, are used to prevent unwanted reflection at surfaces. Such reflection is particularly undesirable in the case of, e.g., cathode ray tubes, liquid crystal displays, and windows because it causes glare and can reduce the brightness and contrast of a displayed image.

Traditional anti-reflective layers have been made from inorganic materials, e.g., magnesium fluoride, that are coated onto an optical element such as a glass lens. Using a quarter-wavelength thick anti-reflective layer can reduce the reflection considerably for the selected wavelength because of destructive interference.

Summary of the Invention

In a first aspect, the invention features an article that includes a plurality of polymer layers, each having a thickness no greater than about 1 micrometer and collectively forming a free-standing film. The layers are selected such that when the article is optically coupled to a surface of a substrate having a refractive index of about 1.50, the article reduces the reflectivity of the substrate at the surface over a wavelength range of interest by a factor of at least about 2 at normal angles of incidence. The article may be optically coupled to the substrate surface, e.g., by adhering it to the substrate surface. Materials are said to be "optically coupled" when the air space between them is replaced by a material with an index of refraction similar to that of the two articles, or when the air space is reduced in thickness to a value much less than a quarter wavelength.

In a second aspect, the invention features an article that includes a plurality of polymer layers, each having a thickness no greater than about 1 micrometer and collectively forming a free-standing film, in which the polymer layers are selected such that the reflectivity measured in air over a wavelength range of interest at normal angles of incidence is no greater than about 6%, preferably no greater than about 3%, and more preferably no greater than about 1%.

In preferred embodiments of the first and second aspects of the invention, the

polymer layers are selected from the group consisting of polymer compositions that are co-extrudable with each other. Examples of suitable polymers include relatively low index polymers such as silicone polymers, fluoropolymers (e.g., a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene terpolymer), fluoro-chloropolymers, methacrylate polymers, polyester copolymers, and combinations thereof, and relatively high index polymers such as polyesters, polycarbonates, polysulfones, polyethersulfones, and combinations thereof. Preferably, the article includes two adjoining polymer layers in which the refractive indices of the adjoining layers are different from each other. At least one polymer layer preferably has an index of refraction less than about 1.55.

The article may further include an inorganic layer. Examples of suitable inorganic layers include zirconia, titania, tin oxide, indium oxide-tin oxide, silver, aluminum, and combinations thereof. The article may also include a layer for modifying the mechanical, chemical, or electrical properties, or combination thereof, of the film.

Each of the polymer layers is preferably oriented in substantially the same direction and to substantially the same degree as the other layers. The article preferably is provided in the form of a flexible film.

In a third aspect, the invention features an article in the form of a free-standing film that includes: (a) a base that includes a polymer layer having a major surface; and (b) an anti-reflective stack optically coupled to the major surface of the base that reduces the reflectivity of the base at the major surface of the base over a first wavelength range of interest. The stack includes alternating layers of (i) high index polymers having an index of refraction greater than about 1.55 and (ii) low index polymers having an index of refraction less than about 1.55. The article may be used to modify the optical properties of a substrate by optically coupling the article to a surface of the substrate, e.g., by adhering the article to the surface.

In preferred embodiments of the third aspect of the invention, the polymer layers of the base and the stack are selected from the group consisting of polymer compositions that are co-extrudable with each other. Examples of suitable polymers for the stack include relatively low index polymers such as silicone polymers, fluoropolymers (e.g., a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene terpolymer), fluoro-chloropolymers, methacrylate polymers, polyester copolymers, and combinations thereof, and relatively high index polymers such as polyesters, polycarbonates, polysulfones,

polyethersulfones, and combinations thereof. Each of the polymer layers of the base and stack is preferably oriented in substantially the same direction and to substantially the same degree as the other layers.

Each of the layers of the stack preferably has a thickness no greater than about 1 micrometer. The particular thickness values for individual layers are chosen using computer modeling and generally fall within the range of about 1/16 wavelength to about 1 wavelength.

The stack may include a polymer layer having a refractive index that is greater than or equal to the highest refractive index of the base. A particularly preferred layer for the stack is a birefringent polymer layer having two orthogonal optic axes parallel to the plane of the film.

The stack may further include an inorganic layer. Examples of suitable inorganic layers include zirconia, titania, tin oxide, indium oxide-tin oxide, silver, aluminum, and combinations thereof. The stack may also include a layer for modifying the mechanical, chemical, or electrical properties, or combination thereof, of the film.

The base may include a pair of opposed major surfaces, each of which is optically coupled to an anti-reflective stack. The base may include a plurality of alternating layers of a first polymer and a second polymer in which the first polymer has a higher index of refraction associated with at least one in-plane axis than adjoining layers of the second polymer. Examples of suitable materials for the first and second polymer include polyethylene naphthalate and a polyethylene naphthalate copolymer, respectively.

In one preferred embodiment, the base includes a multilayer reflective polarizer which selectively reflects light of one polarization and transmits light of a second polarization at normal angles of incidence over a second wavelength range of interest. The polarizer may feature alternating layers of polyethylene naphthalate and a polyethylene naphthalate copolymer.

In another preferred embodiment, the base includes a multilayer mirror that reflects light of two orthogonal polarizations at normal angles of incidence over a second wavelength range of interest. The mirror may feature alternating layers of polyethylene naphthalate and (a) a polyethylene naphthalate copolymer, (b) polymethyl methacrylate, or (c) a terephthalic acid copolymer (e.g., poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate)).

In a fourth aspect, the invention features a process for preparing an article that includes co-extruding a plurality of polymer compositions with each other to form a plurality of polymer layers in the form of a free-standing film, the polymer layers being selected such that when the article is optically coupled to a substrate, the article reduces the reflectivity of the substrate over a wavelength range of interest.

The polymer layers are preferably selected such that when the article is optically coupled to a substrate having a refractive index of about 1.50, the article reduces the reflectivity of the substrate over a wavelength range of interest by a factor of at least about 2. Preferably, the polymer compositions are co-extruded such that each of the resulting polymer layers has a thickness no greater than about 1 micrometer. The polymer compositions are preferably extruded with one or more additional polymer compositions to form one or more removable skin layers on a surface of the article to protect the article.

In a fifth aspect, the invention features a process for preparing an article that includes co-extruding a plurality of polymer compositions with each other to form a plurality of polymer layers in the form of a free-standing film, the polymer layers being selected such that the reflectivity measured in air over a wavelength range of interest at normal angles of incidence is no greater than about 6%, preferably no greater than about 3%, and more preferably no greater than about 1%.

Preferably, the polymer compositions are co-extruded such that each of the resulting polymer layers has a thickness no greater than about 1 micrometer. The polymer compositions are preferably extruded with one or more additional polymer compositions to form one or more removable skin layers on a surface of the article to protect the article.

In a sixth aspect, the invention features a process for preparing an article that includes (a) co-extruding a plurality of polymer compositions with each other to form a free-standing film, where the film includes (i) a base that includes a polymer layer having a major surface, (ii) a precursor anti-reflective construction that includes a polymer layer, and (iii) at least one removable polymer layer; and (b) stretching the film to convert the precursor anti-reflective construction to an anti-reflective construction optically coupled to the major surface of the base and selected to reduce the reflectivity of the base at the major surface over a wavelength range of interest. In some preferred embodiments, the base, the stack, or both, includes a plurality of polymer layers. The process preferably includes the step of stripping the removable polymer layer from the film prior to stretching the film; the

removable polymer layer may also be removed subsequent to stretching the film. Examples of preferred materials for the removable polymer layer include polyethylene, polypropylene, atactic polystyrene, and combinations thereof.

The invention provides lightweight, relatively inexpensive, polymeric anti-reflective constructions that can be used alone or in combination with a number of materials, including multilayer polymeric polarizers and mirrors. The structure and properties of the anti-reflective construction can be tailored to render it effective over a selected portion of the electromagnetic spectrum. In addition, unlike conventional vacuum-deposited anti-reflective coatings, the polymeric anti-reflective constructions according to the invention can readily be aplied to non-planar (e.g., curved) surfaces such as cathode ray tubes.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Brief Description of the Drawings

FIG. 1A is a schematic sectional view of an article featuring a base optically coupled to a single-layer anti-reflective ("AR") construction.

FIG. 1B is a schematic sectional view of an article featuring a base optically coupled to a single-layer AR construction, in which a removable skin layer is positioned over the AR construction.

FIG. 2A is a schematic sectional view of an article featuring a base optically coupled to a multilayer AR construction.

FIG. 2B is a schematic sectional view of an article featuring a pair of bases, each optically coupled to a multilayer AR construction, in which the two structures are separated by an internal skin layer.

FIG. 3 is a plot of reflectivity versus wavelength for a PET base optically coupled to a 4-layer THV/PEN AR construction calculated at 0E relative to the normal (curve a) and 60E relative to the normal for s polarized light (curve s) and p polarized light (curve p).

FIG. 4 is a schematic sectional view of an article featuring a base provided with an optical coupling agent for attachment to a substrate, in which the base is further optically coupled to a multilayer AR construction.

FIG. 5 is a schematic sectional view of an article featuring a multilayer base provided with a plurality of anti-reflective stacks separated by skin layers.

FIG. 6 is a plot of reflectivity versus wavelength for a PET base optically coupled to a 44-layer PEN/PMMA AR construction calculated at 0E relative to the normal.

FIG. 7 is a plot of transmission versus wavelength for a glass base optically coupled to an 81-layer THV/PMMA-PVDF/PC construction, where the PMMA-PVDF acts as a tie layer.

Figure 8 is a graphical view illustrating the refractive indices characteristics of the PEN and coPEN layers of the present invention.

Figure 9 is a graphical view of computer simulated data of percent transmission of a 50-layer Pen/coPEN film stack based on the indices shown in Figure 8.

Figure 10 is a graphical view of computer simulated data of percent transmission of an equally biaxially stretched 300-layer PEN/coPET mirror.

Figure 11 is a graphical view of percent measured transmission of a 51-layer I.R. polarizer of the present invention with the first order peak near 1,300 nm.

Figure 12 is a graphical view of percent measured transmission of eight 51-layer polarizers of the present invention laminated together.

Figure 13 is a graphical view of percent measured transmission of a 204-layer polarizer of the present invention.

Figure 14 is a graphical view of percent measured transmission of two 204-layer polarizers of the present invention laminated together.

Figures 15 and 16 show reflectivity versus angle curves for a uniaxial birefringent system in a medium of index 1.60.

Figure 17 shows reflectivity versus angle curves for a uniaxial birefringent system in a medium of index 1.0

Figures 18, 19 and 20 show various relationships between in-plane indices and z-index for a uniaxial birefringent system.

Figure 21 shows off axis reflectivity versus wavelength for two different biaxial birefringent systems.

Figure 22 shows the effect of introducing a y-index difference in a biaxial birefringent film with a large z-index difference.

Figure 23 shows the effect of introducing a y-index difference in a biaxial

birefringent film with a smaller z-index difference.

Figure 24 shows a contour plot summarizing the information from Figures 22 and 23.

Figures 25a and 25b are diagrammatical views of the polarizer of the present invention.

Figure 26 shows a two layer stack of films forming a single interface.

Description of the Preferred Embodiments Structure

Anti-reflective (AR) constructions are preferably provided in the form of free-standing films, i.e., films having sufficient mechanical integrity that they can be readily handled without the need for additional reinforcing layers. The anti-reflective properties can be tailored to cover a selected range of electromagnetic frequencies, including portions of the visible, infrared (IR), and ultraviolet (UV) regions of the electromagnetic spectrum.

The AR constructions may be used alone (such that the film forms an interface with air) or optically coupled to one or both major surfaces of a base; in the latter case, the AR construction de-reflects radiation impinging upon the surface of the base at the base/AR construction interface. The AR construction may be adhered to the surface of the base. Preferably, however, it is formed simultaneously with the base by co-extrusion, as described in more detail, below. In addition, the base/AR construction article may itself be optically coupled, e.g., by means of an adhesive to yet another surface, e.g., a window.

The AR construction may consist of any number of polymer layers, typically ranging from one to several tens of layers. The AR polymer layers may be optically thin, e.g., with a thickness of between about 0.010 μm and about 0.25 μm, or optically thick, e.g., with a thickness of greater than about 0.25 μm, or a combination of optically thin and optically thick layers. The particular thickness values are selected depending upon the portion of the electromagnetic spectrum over which the film is designed to operate and, where the AR construction is optically coupled to a base, the optical characteristics of the base. The AR polymer layers are preferably made from polymer compositions that are co-extrudable with each other and, where the AR construction is optically coupled to a base, the materials forming the base.

An example of a single layer AR construction is schematically shown in Figure 1A. As shown in the figure, article 100 features a base 102 and an anti-reflective polymer

layer 104. AR layer 104 (which may be optically thick or thin) preferably is made from a thermoplastic polymer with a lower index of refraction than base 102. Specifically, reflection is minimized when AR layer 104 has an index of refraction that is approximately the square root of a multiple of the index of refraction of the base and the surrounding medium (e.g. air), and is a quarter wavelength thick. Preferred polymers for AR layer 104 typically have an index of refraction less than about 1.45, more preferably less than about 1.38.

Suitable low index polymers for AR layer 104 include silicone polymers, methacrylate polymers, fluoropolymers, polyester copolymers, and fluoro-chloropolymers. Particularly preferred are fluoropolymers available under the trade designation THV-500 from Dyneon LLC, St. Paul, MN, a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene terpolymer which has an index of refraction of 1.36, in the form of quarter wavelength layers on the base. These polymers can reduce the total surface reflectivity of a relatively high index of refraction base by about a factor of 2 irrespective of layer thickness. As a specific example, biaxially oriented polyethylene terephthalate (PET) has an index of refraction of 1.66 and reflectivity for visible light of 6.0% per surface at a normal angle of incidence. Covering such a biaxially oriented PET base with an optically thick layer of THV-500 fluoropolymer will reduce the reflectivity of the combined film to a calculated value of about 3.26% per side. Reflectivity would be reduced even further if the THV layer were a quarter wavelength thick.

To lower the reflectivity even further, it may be preferable to use a thin film, multilayer AR construction. Such constructions offer the advantage of improved broad band reduction in reflectivity relative to single-layer AR constructions while maintaining acceptable bandwidths. A multilayer AR construction is shown in Figure 2A. With reference to Figure 2A, an article 130 features a base 134 provided on two sides with a multilayer AR stack 132; it is also possible to provide the AR stack on only one side of the base. Each layer 136 of the AR stack 132 will generally be optically thin, although optically thick layers, or a combination of optically thin and optically thick layers, can be used as well.

AR stacks 132 can consist of any number of material layers 136 depending on the optical characteristics of the base and the desired portion of the electromagnetic spectrum over which AR stacks 132 are designed to operate. Stacks having two or more

layers can produce lower reflectivity over a wider band than a single layer, especially if the base has an index of refraction below about 1.60. With multiple layers in the AR stack, reflections from multiple interfaces can destructively interfere to reduce the overall reflectivity.

One of the materials in a multilayer AR stack preferably has an index equal to or higher than that of the highest index of refraction associated with the base. Since a multilayer stack of only two materials can be designed to function as an equivalent single layer of almost any index, AR stacks having four or more layers can be made using only two materials, and have a wider bandwidth than a three material, three-layer stack. This is useful in the case of articles prepared by co-extrusion (as described below) because in the co-extrusion process it is easier to add extra layers of existing materials than to add a new material. Suitable materials for the AR layers include thermoplastic polymers such as, for example, polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, 2,6-polybutylene naphthalate, polyamides, polycarbonates, atactic polystyrene, syndiotactic polystyrene, and polymethyl methacrylate. Copolymers based upon these materials may also be suitable.

Layers having different refractive indices may be separated by "tie layers" having indices intermediate those of surrounding layers. Such layers are particularly useful for improving the adhesion between layers in the stack. An example of such a construction features, in order of decreasing index of refraction, polycarbonate/polymethyl methacrylate/polyvinylidene fluoride/THV fluoropolymer, where the polymethyl methacrylate and polyvinylidene fluoride act as a tie layer to improve the adhesion between the polycarbonate and the THV fluoropolymer.

Figure 7 illustrates calculated transmission values for an eighty one layer AR construction utilizing polycarbonate ("PC") and THV fluoropolymer as the high and low index layers, respectively, on a glass substrate, with polymethyl methacrylate ("PMMA")-polyvinylidene fluoride ("PVDF") acting as a tie layer. The refractive index of the tie layer was allowed to float between 1.45 and 1.55, and ended with an optimized index of 1.497. The stack was optimized to anti-reflect a glass surface. As shown in Figure 7, a significant anti-reflective effect was obtained.

Particularly preferred articles include those in which one or more of the AR stack layers 136 is made of the same material or materials as the base 134, or as one or

more layers of the base. For example, if a multilayer base film is to be de-reflected over a portion of the wavelength spectrum, e.g., in the case of a base functioning as an IR mirror provided with an AR construction designed to de-reflect visible light, it would be desirable to design the AR stack from the same materials as the mirror itself.

Another example of a useful article is one featuring a multilayer AR construction combining both polymer layers and layers of higher index inorganic materials.

In one embodiment, the inorganic material would have an index of refraction intermediate that of the base and the organic polymer. For example, the inorganic material could be a sol gel-deposited layer of alumina or a zirconia-silica mix on a PEN base and the organic polymer could be a fluoropolymer such as THV-500.

In another embodiment, the inorganic material would have an index of refraction higher than that of the base. For example, the inorganic material could be a sol gel-deposited layer of zirconia or titania on a PEN base and the organic polymer could be a quarter wavelength thick fluoropolymer such as THV-500.

In another embodiment, the inorganic material could be silver, aluminum, or a quarter or half wavelength thick layer of a transparent conductor such as indium-tin oxide (ITO) having far IR rejection capabilities, and the polymer layer could be a quarter wavelength thick fluoropolymer such as THV-500.

In yet another embodiment, the inorganic material could be combined with a multilayer polymer construction.

Materials useful for the base include both organic polymers and inorganic materials such as ceramics and glasses having relatively high refractive indices. Particularly preferred base materials are single and multilayer polymer films. Examples of suitable single layer polymer films include polyethylene terephthalate and polycarbonate films; such films, in turn, may be uniaxially or biaxially oriented. One example of a suitable multilayer polymer film is one in which the thickness of the individual polymer layers is no greater than about 0.5 micrometers, as described in Wheatley et al., U.S. 5,278,694.

A second example of a suitable multilayer polymer film is described in commonly assigned U.S. Patent Application Serial No. 08/402,041. Very briefly, that application describes the construction of multilayer polymer films (mirrors and polarizers)

for which the Brewster angle (the angle at which reflectance goes to zero) is very large or is nonexistent for the polymer layer interfaces. This allows for the construction of multilayer mirrors and polarizers whose reflectivity for p polarized light decreases slowly with angle of incidence, is independent of angle of incidence, or increases with angle of incidence away from the normal. As a result, multilayer films having high reflectivity for both s and p polarized light over a wide bandwidth, and over a wide range of angles can be achieved.

The relationships between the indices of refraction in each film layer of the base to each other determine the reflectance behavior of the base at any angle of incidence, from any azimuthal direction. The principles and design considerations described in U.S. Patent Application 08/402,041 can be applied to create multilayer bases having the desired optical effects for a wide variety of circumstances and applications. The indices of refraction of the layers in the multilayer base can be manipulated and tailored to produce devices having the desired optical properties. Many useful devices, such as mirrors and polarizers having a wide range of performance characteristics, can be designed and fabricated using the principles described therein.

Particularly preferred combinations of layers in the case of polarizers include polyethylene naphthalate ("PEN")/coPEN, polyethylene terephthalate ("PET")/coPEN, PEN/syndiotactic polystyrene ("SPS"), PET/SPS, PEN/Estar, and PET/Estar, where "coPEN" refers to a copolymer or blend based upon naphthalene dicarboxylic acid, and "Estar" is a trade designation for a copolymerof terephthalic acid, ethylene glycol, and cyclohexane-1,4-dimethanol that is commercially available from Eastman Chemical Co., Kingsport, TN.

Particularly preferred combinations of layers in the case of mirrors include PET/Ecdel, PEN/Ecdel, PEN/SPS, PEN/THV, PEN/polymethyl methacrylate ("PMMA"), PEN/coPET, and PET/SPS, where "coPET" refers to a copolymer or blend based upon terephthalic acid (as described above), "Ecdel" is a trade designation for a copolymer of cyclohexane dicarboxylic acid, ethylene glycol, and cyclohexane-1,4-dimethanol that is commercially available from Eastman Chemical Co., Kingsport, TN.

PEN is a preferred material because of its high positive stress optical coefficient and permanent birefringence after stretching, with the refractive index for polarized incident light of 550 nm wavelength increasing when the plane of polarization is parallel

to the stretch direction from about 1.64 to as high as about 1.9. The differences in refractive indices associated with different in-plane axes exhibited by PEN and a 70-naphthalate/30- terephthalate copolyester (coPEN) for a 5:1 stretch ratio are illustrated in Figure 8. In Figure 8, the data on the lower curve represent the index of refraction of PEN in the transverse direction and the coPEN while the upper curve represents the index of refraction of PEN in the stretch direction. PEN exhibits a difference in refractive index of 0.25 to 0.40 in the visible spectrum. The birefringence (difference in refractive index) can be increased by increasing the molecular orientation. PEN is heat stable from about 155°C up to about 230°C depending upon shrinkage requirements of the application. Although PEN has been specifically discussed above as the preferred polymer for the birefringent layer, polybutylene naphthalate is also a suitable material as well as other crystalline naphthalene dicarboxylic polyesters. The crystalline naphthalene dicarboxylic polyester should exhibit a difference in refractive indices associated with different in-plane axes of at least 0.05 and preferably above 0.20.

Minor amounts of comonomers may be substituted into the naphthalene dicarboxylic acid polyester so long as the high refractive index in the stretch direction(s) is not substantially compromised. A drop in refractive index (and therefore decreased reflectivity) may be counter balanced by advantages in any of the following: adhesion to the selected polymer layer, lowered temperature of extrusion, better match of melt viscosities, better match of glass transition temperatures for stretching. Suitable monomers include those based on isophthalic, azelaic, adipic, sebacic, dibenzoic, terephthalic, 2,7- naphthalene icarboxylic, 2,6-naphthalene dicarboxylic or cyclohexanedicarboxylic acids.

The PEN/selected polymer resins of the present invention preferably have similar melt viscosities so as to obtain uniform multilayer coextrusion. The two polymers preferably have a melt viscosity within a factor of 5 at typical shear rates.

The PEN and the preferred selected polymer layers of the present invention exhibit good adhesion properties to each other while still remaining as discrete layers within the multilayered sheet.

The glass transition temperatures of the polymers of the present invention are compatible so adverse effects such as cracking of one set of polymer layers during stretching does not occur. By compatible is meant that the glass transition temperature of

the selected polymer is lower than the glass transition temperature of the PEN layer. The glass transition temperature of the selected polymer layer temperature may be slightly higher than the glass transition temperature of the PEN layer, but by no more than 40°C.

Preferably, the layers have a 1/4 wavelength thickness with different sets of layers designed to reflect different wavelength ranges. Each layer does not have to be exactly 1/4 wavelength thick. The overriding requirement is that the adjacent low-high index film pair have a total optical thickness of 0.5 wavelength. The bandwidth of a 50-layer stack of PEN/coPEN layers having the index differential indicated in Figure 8, with layer thicknesses chosen to be a 1/4 wavelength of 550 nm, is about 50 nm. This 50-layer stack provides roughly a 99 percent average reflectivity in this wavelength range with no measurable absorption. A computer-modeled curve showing less than 1 percent transmission (99 percent reflectivity) is illustrated in Figure 9. Figures 9-17 include data characterized as percent transmission. It should be understood that since there is no measurable absorbance by the film of the present invention that percent reflectivity is approximated by the following relationship:

100 - (percent transmission) = (percent reflectivity)

The preferred selected polymer layer 14 remains isotropic in refractive index and substantially matches the refractive index of the PEN layer associated with the transverse axis as illustrated in Figure 25a. Light with its plane of polarization in this direction will be predominantly transmitted by the polarizer while light with its plane of polarization in the oriented direction will be reflected as illustrated in Figure 25b.

Orientation of the extruded film was done by stretching individual sheets of the material in heated air. For economical production, stretching may be accomplished on a continuous basis in a standard length orienter, tenter oven, or both. Economies of scale and line speeds of standard polymer film production may be achieved thereby achieving manufacturing costs that are substantially lower than costs associated with commercially available absorptive polarizers.

Lamination of two or more sheets together is advantageous, to improve reflectivity or to broaden the bandwidth, or to form a mirror from two polarizers. Amorphous copolyesters are useful as laminating materials, and those with trade designations VITEL

3000 and 3300 from the Goodyear Tire and Rubber Co. of Akron, Ohio, are noted as materials that have been tried. The choice of laminating material is broad, with adhesion to the sheets 10, optical clarity and exclusion of air being the primary guiding principles.

It may be desirable to add to one or more of the layers, one or more inorganic or organic adjuvants such as an antioxidant, extrusion aid, heat stabilizer, ultraviolet ray absorber, nucleator, surface projection forming agent, and the like in normal quantities so long as the addition does not substantially interfere with the performance of the present invention.

The optical behavior of a multilayer stack 10 such as that shown above in Figs. 25a and 25b will now be described in more general terms.

The optical properties and design considerations of multilayer stacks described below allow the construction of multilayer stacks for which the Brewster angle (the angle at which reflectance goes to zero) is very large or is nonexistent. This allows for the construction of multilayer mirrors and polarizers whose reflectivity for p polarized light decrease slowly with angle of incidence, are independent of angle of incidence, or increase with angle of incidence away from the normal. As a result, multilayer stacks having high reflectivity for both s and p polarized light over a wide bandwidth, and over a wide range of angles can be achieved.

The average transmission at normal incidence for a multilayer stack, (for light polarized in the plane of the extinction axis in the case of polarizers, or for both polarizations in the case of mirrors), is desirably less than 50 % (reflectivity of 0.5) over the intended bandwidth. (It shall be understood that for the purposes of the present application, all transmission or reflection values given include front and back surface reflections). Other multilayer stacks exhibit lower average transmission and/or a larger intended bandwidth, and/or over a larger range of angles from the normal. If the intended bandwidth is to be centered around one color only, such as red, green or blue, each of which has an effective bandwidth of about 100 nm each, a multilayer stack with an average transmission of less than 50% is desirable. A multilayer stack having an average transmission of less than 10% over a bandwidth of 100 nm is also preferred. Other exemplary preferred mutlilayer stacks have an average transmission of less than 30% over a bandwidth of 200 nm. Yet another preferred multilayer stack exhibits an average transmission of less than 10% over the bandwidth of the visible spectrum (400-700 nm).

Most preferred is a multilayer stack that exhibits an average transmission of less than 10% over a bandwidth of 380 to 740 nm. The extended bandwidth is useful even in visible light applications in order to accommodate spectral shifts with angle, and variations in the multilayer stack and overall film caliper.

The multilayer stack 10 can include tens, hundreds or thousands of layers, and each layer can be made from any of a number of different materials. The characteristics which determine the choice of materials for a particular stack depend upon the desired optical performance of the stack.

The stack can contain as many materials as there are layers in the stack. For ease of manufacture, preferred optical thin film stacks contain only a few different materials. For purposes of illustration, the present discussion will describe multilayer stacks including two materials.

The boundaries between the materials, or chemically identical materials with different physical properties, can be abrupt or gradual. Except for some simple cases with analytical solutions, analysis of the latter type of stratified media with continuously varying index is usually treated as a much larger number of thinner uniform layers having abrupt boundaries but with only a small change in properties between adjacent layers.

Several parameters may affect the maximum reflectivity achievable in any multilayer stack. These include basic stack design, optical absorption, layer thickness control and the relationship between indices of refraction of the layers in the stack. For high reflectivity and/or sharp bandedges, the basic stack design should incorporate optical interference effects using standard thin film optics design. This typically involves using optically thin layers, meaning layers having an optical thickness in the range of 0.1 to 1.0 times the wavelength of interest. The basic building blocks for high reflectivity multilayer films are low/high index pairs of film layers, wherein each low/high index pair of layers has a combined optical thickness of 1/2 the center wavelength of the band it is designed to reflect. Stacks of such films are commonly referred to as quarterwave stacks.

To minimize optical absorption, the preferred multilayer stack ensures that wavelengths that would be most strongly absorbed by the stack are the first wavelengths reflected by the stack. For most clear optical materials, including most polymers, absorption increases toward the blue end of the visible spectrum. Thus, it is preferred to tune the multilayer stack such that the "blue" layers are on the incident side of the

multilayer stack.

A multilayer construction of alternative low and high index thick films, often referred to as a "pile of plates", has no tuned wavelengths nor bandwidth constraints, and no wavelength is selectively reflected at any particular layer in the stack. With such a construction, the blue reflectivity suffers due to higher penetration into the stack, resulting in higher absorption than for the preferred quarterwave stack design. Arbitrarily increasing the number of layers in a "pile of plates" will not always give high reflectivity, even with zero absorption. Also, arbitrarily increasing the number of layers in any stack may not give the desired reflectivity, due to the increased absorption that would occur.

The relationships between the indices of refraction in each film layer to each other and to those of the other layers in the film stack determine the reflectance behavior of the multilayer stack at any angle of incidence, from any azimuthal direction. Assuming that all layers of the same material have the same indices, then a single interface of a two component quarterwave stack can be analyzed to understand the behavior of the entire stack as a function of angle.

For simplicity of discussion, therefore, the optical behavior of a single interface will be described. It shall be understood, however, that an actual multilayer stack according to the principles described herein could be made of tens, hundreds or thousands of layers. To describe the optical behavior of a single interface, the reflectivity as a function of angle of incidence for s and p polarized light for a plane of incidence including the z-axis and one in-plane optic axis will be plotted.

Fig. 26 shows two material film layers forming a single interface, with both immersed in an isotropic medium of index no. For simplicity of illustration, the present discussion will be directed toward an orthogonal multilayer birefringent system with the optical axes of the two materials aligned, and with one optic axis (z) perpendicular to the film plane, and the other optic axes along the x and y axis. It shall be understood, however, that the optic axes need not be orthogonal, and that nonorthogonal systems are well within the spirit and scope of the present invention. It shall be further understood that the optic axes also need not be aligned with the film axes to fall within the intended scope of the present invention.

The reflectivity of a dielectric interface varies as a function of angle of incidence, and for isotropic materials, is different for p and s polarized light. The reflectivity

minimum for p polarized light is due to the so called Brewster effect, and the angle at which the reflectance goes to zero is referred to as Brewster's angle.

The reflectance behavior of any film stack, at any angle of incidence, is determined by the dielectric tensors of all films involved. A general theoretical treatment of this topic is given in the text by R.M.A. Azzam and N.M. Bashara, Ellipsometry and Polarized Light, published by North-Holland, 1987.

The reflectivity for a single interface of a system is calculated by squaring the absolute value of the reflection coefficients for p and s polarized light, given by equations 1 and 2, respectively. Equations 1 and 2 are valid for uniaxial orthogonal systems, with the axes of the two components aligned.

$$1)\quad r_{pp} = \frac{n2z * n2o \sqrt{(n1z2 - nosin2\theta)} - n1z * n1o \sqrt{(n2z2 - nosin2\theta)}}{n2z * n2o \sqrt{(n1z2 - nosin2\theta)} + n1z * n1o \sqrt{(n2z2 - nosin2\theta)}}$$

$$2)\quad r_{ss} = \frac{\sqrt{(n1o2 - nosin2\theta)} - \sqrt{(n2o2 - nosin2\theta)}}{\sqrt{(n1o2 - nosin2\theta)} + \sqrt{(n2o2 - nosin2\theta)}}$$

where θ is measured in the isotropic medium.

In a uniaxial birefringent system, n1x = n1y = n1o, and n2x = n2y = n2o.

For a biaxial birefringent system, equations 1 and 2 are valid only for light with its plane of polarization parallel to the x-z or y-z planes, as defined in Fig. 26. So, for a biaxial system, for light incident in the x-z plane, n1o = n1x and n2o = n2x in equation 1 (for p-polarized light), and n1o = n1y and n2o = n2y in equation 2 (for s-polarized light). For light incident in the y-z plane, n1o = n1y and n2o = n2y in equation 1 (for p-polarized light), and n1o = n1x and n2o = n2x in equation 2 (for s-polarized light).

Equations 1 and 2 show that reflectivity depends upon the indices of refraction in the x, y (in-plane) and z directions of each material in the stack. In an isotropic material, all three indices are equal, thus nx = ny = nz. The relationship between nx, ny and nz determine the optical characteristics of the material. Different relationships between the three indices lead to three general categories of materials: isotropic, uniaxially birefringent, and biaxially birefringent. Equations 1 and 2 describe biaxially birefringent cases only

along the x or y axis, and then only if considered separately for the x and y directions.

A uniaxially birefringent material is defined as one in which the index of refraction in one direction is different from the indices in the other two directions. For purposes of the present discussion, the convention for describing uniaxially birefringent systems is for the condition $nx = ny \neq nz$. The x and y axes are defined as the in-plane axes and the respective indices, nx and ny, will be referred to as the in-plane indices.

One method of creating a uniaxial birefringent system is to biaxially stretch (e.g., stretch along two dimensions) a multilayer stack in which at least one of the materials in the stack has its index of refraction affected by the stretching process (e.g., the index either increases or decreases). Biaxial stretching of the multilayer stack may result in differences between refractive indices of adjoining layers for planes parallel to both axes thus resulting in reflection of light in both planes of polarization.

A uniaxial birefringent material can have either positive or negative uniaxial birefringence. Positive uniaxial birefringence occurs when the z-index is greater than the in-plane indices ($nz > nx$ and ny). Negative uniaxial birefringence occurs when the z-index is less than the in-plane indices ($nz < nx$ and ny).

A biaxial birefringent material is defined as one in which the indices of refraction in all three axes are different, e.g., $nx \neq ny \neq nz$. Again, the nx and ny indices will be referred to as the in-plane indices. A biaxial birefringent system can be made by stretching the multilayer stack in one direction. In other words the stack is uniaxially stretched. For purposes of the present discussion, the x direction will be referred to as the stretch direction for biaxial birefringent stacks.

To make a mirror, two uniaxially stretched polarizing sheets 10 are positioned with their respective orientation axes rotated 90°, or the sheet 10 is biaxially stretched. In the latter case, both PEN refractive indices in the plane of the sheet increase and the selected polymer should be chosen with as low of a refractive index as possible to reflect light of both planes of polarization. Biaxially stretching the multilayered sheet will result in differences between refractive indices of adjoining layers for planes parallel to both axes thereby resulting in reflection of light in both planes of polarization directions. Biaxially stretching PEN will increase the refractive indices associated with those axes of elongation from 1.64 to only 1.75, compared to the uniaxial value of 1.9. Therefore to create a dielectric mirror with 99 percent reflectivity (and thus with no noticeable iridescence) a

low refractive index coPET is preferred as the selected polymer. Optical modeling indicates this is possible with an index of about 1.55. A 300-layer film with a 5 percent standard deviation in layer thickness, designed to cover half of the visible spectrum with six overlapping quarterwave stacks, has the predicted performance shown in Figure 10. A greater degree of symmetry of stretching yields an article that exhibits relatively more symmetric reflective properties and relatively less polarizing properties.

If desired, two or more sheets of the invention may be used in a composite to increase reflectivity, optical bandwidth, or both. If the optical thicknesses of pairs of layers within the sheets are substantially equal, the composite will reflect, at somewhat greater efficiency, substantially the same band width and spectral range of reflectivity (i.e., "band") as the individual sheets. If the optical thicknesses of pairs of layers within the sheets are not substantially equal, the composite will reflect across a broader bandwidth than the individual sheets. A composite combining mirror sheets with polarizer sheets is useful for increasing total reflectance while still polarizing transmitted light. Alternatively, a single sheet may be asymmetrically biaxially stretched to produce a film having selective reflective and polarizing properties.

The preferred selected polymer for use in a biaxially stretched mirror application is based on terephthalic, isophthalic, sebacic, azelaic or cyclohexanedicarboxylic acid to attain the lowest possible refractive index while still maintaining adhesion to the PEN layers. Naphthalene dicarboxylic acid may still be employed in minor amounts to improve the adhesion to PEN. The diol component may be taken from any that have been previously mentioned. Preferably the selected polymer has an index of refraction of less than 1.65 and more preferably an index of refraction of less than 1.55.

It is not required that the selected polymer be a copolyester or copolycarbonate. Vinyl polymers and copolymers made from monomers such as vinyl naphthalenes, styrenes, ethylene, maleic anhydride, acrylates, methacrylates, might be employed. Condensation polymers other than polyesters and polycarbonates might also be useful, examples include: polysulfones, polyamides, polyurethanes, polyamic acids, polyimides. Naphthalene groups and halogens such as chlorine, bromine and iodine are useful in increasing the refractive index of the selected polymer to the desired level (1.59 to 1.69) to substantially match the refractive index of PEN associated with the transverse direction for a polarizer. Acrylate groups and fluorine are particularly useful in decreasing refractive

index for use in a mirror.

The optical properties and design considerations of uniaxial birefringent systems will now be discussed. As discussed above, the general conditions for a uniaxial birefringent material are $nx = ny \neq nz$. Thus if each layer 102 and 104 in Fig. 26 is uniaxially birefringent, $n1x = n1y$ and $n2x = n2y$. For purposes of the present discussion, assume that layer 102 has larger in-plane indices than layer 104, and that thus $n1 > n2$ in both the x and y directions. The optical behavior of a uniaxial birefringent multilayer system can be adjusted by varying the values of $n1z$ and $n2z$ to introduce different levels of positive or negative birefringence. The relationship between the various indices of refraction can be measured directly, or, the general relationship may be indirectly observed by analysis of the spectra of the resulting film as described herein.

In the case of mirrors, the desired average transmission for light of each polarization and plane of incidence generally depends upon the intended use of the mirror. The average transmission along each stretch direction at normal incidence for a narrow bandwidth mirror across a 100 nm bandwidth within the visible spectrum is desirably less than 30%, preferably less than 20% and more preferably less than 10%. A desirable average transmission along each stretch direction at normal incidence for a partial mirror ranges anywhere from, for example, 10% to 50%, and can cover a bandwidth of anywhere between, for example, 100 nm and 450 nm, depending upon the particular application. For a high efficiency mirror, average transmission along each stretch direction at normal incidence over the visible spectrum (400-700nm) is desirably less than 10%, preferably less than 5%, more preferably less than 2%, and even more preferably less than 1%. In addition, asymmetric mirrors may be desirable for certain applications. In that case, average transmission along one stretch direction may be desirably less than, for example, 50%, while the average transmission along the other stretch direction may be desirably less than, for example 20%, over a bandwidth of, for example, the visible spectrum (400-700 nm), or over the visible spectrum and into the near infrared (e.g, 400-850 nm).

Equation 1 described above can be used to determine the reflectivity of a single interface in a uniaxial birefringent system composed of two layers such as that shown in Fig. 26. Equation 2, for s polarized light, is identical to that of the case of isotropic films ($nx = ny = nz$), so only equation 1 need be examined. For purposes of illustration, some specific, although generic, values for the film indices will be assigned. Let $n1x = n1y =$

1.75, n1z = variable, n2x = n2y = 1.50, and n2z = variable. In order to illustrate various possible Brewster angles in this system, no = 1.60 for the surrounding isotropic media.

Fig. 15 shows reflectivity versus angle curves for p-polarized light incident from the isotropic medium to the birefringent layers, for cases where n1z is numerically greater than or equal to n2z (n1z • n2z). The curves shown in Fig. 15 are for the following z-index values: a) n1z =1.75, n2z = 1.50; b) n1z = 1.75, n2z = 1.57; c) n1z = 1.70, n2z = 1.60; d) n1z = 1.65, n2z = 1.60; e) n1z = 1.61, n2z = 1.60; and f) n1z = 1.60 = n2z. As n1z approaches n2z, the Brewster angle, the angle at which reflectivity goes to zero, increases. Curves a - e are strongly angular dependent. However, when n1z = n2z (curve f), there is no angular dependence to reflectivity. In other words, the reflectivity for curve f is constant for all angles of incidence. At that point, equation 1 reduces to the angular independent form: (n2o - n1o)/(n2o + n1o). When n1z = n2z, there is no Brewster effect and there is constant reflectivity for all angles of incidence.

Fig. 16 shows reflectivity versus angle of incidence curves for cases where n1z is numerically less than or equal to n2z. Light is incident from isotropic medium to the birefringent layers. For these cases, the reflectivity monotonically increases with angle of incidence. This is the behavior that would be observed for s-polarized light. Curve a in Fig. 16 shows the single case for s polarized light. Curves b-e show cases for p polarized light for various values of nz, in the following order: b) n1z =1.50, n2z = 1.60; c) n1z = 1.55, n2z = 1.60; d) n1z =1.59, n2z = 1.60; and e) n1z = 1.60 = n2z. Again, when n1z = n2z (curve e), there is no Brewster effect, and there is constant reflectivity for all angles of incidence.

Fig. 17 shows the same cases as Fig. 15 and 16 but for an incident medium of index no =1.0 (air). The curves in Fig. 17 are plotted for p polarized light at a single interface of a positive uniaxial material of indices n2x = n2y = 1.50, n2z = 1.60, and a negative uniaxially birefringent material with n1x = n1y = 1.75, and values of n1z, in the following order, from top to bottom, of: a) 1.50; b) 1.55; c) 1.59; d) 1.60; f) 1.61; g) 1.65; h) 1.70; and i) 1.75. Again, as was shown in Figs. 15 and 16, when the values of n1z and n2z match (curve d), there is no angular dependence to reflectivity.

Figs. 15, 16 and 17 show that the cross-over from one type of behavior to another occurs when the z-axis index of one film equals the z-axis index of the other film. This is true for several combinations of negative and positive uniaxially birefringent, and isotropic

materials. Other situations occur in which the Brewster angle is shifted to larger or smaller angles.

Various possible relationships between in-plane indices and z-axis indices are illustrated in Figs. 18, 19 and 20. The vertical axes indicate relative values of indices and the horizontal axes are used to separate the various conditions. Each Figure begins at the left with two isotropic films, where the z-index equals the in-plane indices. As one proceeds to the right, the in-plane indices are held constant and the various z-axis indices increase or decrease, indicating the relative amount of positive or negative birefringence.

The case described above with respect to Figs. 15, 16 and 17 is illustrated in Fig. 18. The in-plane indices of material one are greater than the in-plane indices of material two, material 1 has negative birefringence (n1z less than in-plane indices), and material two has positive birefringence (n2z greater than in-plane indices). The point at which the Brewster angle disappears and reflectivity is constant for all angles of incidence is where the two z-axis indices are equal. This point corresponds to curve f in Fig. 15, curve e in Fig. 16 or curve d in Fig. 17.

In Fig. 19, material one has higher in-plane indices than material two, but material one has positive birefringence and material two has negative birefringence. In this case, the Brewster minimum can only shift to lower values of angle.

Both Figs. 18 and 19 are valid for the limiting cases where one of the two films is isotropic. The two cases are where material one is isotropic and material two has positive birefringence, or material two is isotropic and material one has negative birefringence. The point at which there is no Brewster effect is where the z-axis index of the birefringent material equals the index of the isotropic film.

Another case is where both films are of the same type, i.e., both negative or both positive birefringent. Fig. 20 shows the case where both films have negative birefringence. However, it shall be understood that the case of two positive birefringent layers is analogous to the case of two negative birefringent layers shown in Fig. 20. As before, the Brewster minimum is eliminated only if one z-axis index equals or crosses that of the other film.

Yet another case occurs where the in-plane indices of the two materials are equal, but the z-axis indices differ. In this case, which is a subset of all three cases shown in Figs. 18-20, no reflection occurs for s polarized light at any angle, and the reflectivity for p

polarized light increases monotonically with increasing angle of incidence. This type of article has increasing reflectivity for p-polarized light as angle of incidence increases, and is transparent to s-polarized light. This article can be referred to as a "p-polarizer".

The above described principles and design considerations describing the behavior of uniaxially birefringent systems can be applied to create multilayer stacks having the desired optical effects for a wide variety of circumstances and applications. The indices of refraction of the layers in the multilayer stack can be manipulated and tailored to produce devices having the desired optical properties. Many negative and positive uniaxial birefringent systems can be created with a variety of in-plane and z-axis indices, and many useful devices can be designed and fabricated using the principles described here.

The reflective polarizer of the present invention is useful in optical elements such as ophthalmic lenses, mirrors and windows. The polarizer is characterized by a mirror-like look which is considered stylish in sunglasses. In addition, PEN is a very good ultraviolet filter, absorbing ultraviolet efficiently up to the edge of the visible spectrum. The reflective polarizer of the present invention would also be useful as a thin infrared sheet polarizer.

For the polarizer, the sheet is preferably oriented by stretching in a single direction and the index of refraction of the PEN layer exhibits a large difference between incident light rays with the plane of polarization parallel to the oriented and transverse directions. The index of refraction associated with an in-plane axis (an axis parallel to the surface of the film) is the effective index of refraction for plane-polarized incident light whose plane of polarization is parallel to that axis. By oriented direction is meant the direction in which the film is stretched. By transverse direction is meant that direction orthogonal in the plane of the film to the direction in which the film is oriented.

For the polarizer, the PEN/selected polymer layers have at least one axis for which the associated indices of refraction are preferably substantially equal. The match of refractive indices associated with that axis, which typically is the transverse axis, results in substantially no reflection of light in that plane of polarization. The selected polymer layer may also exhibit a decrease in the refractive index associated with the stretch direction. A negative birefringence of the selected polymer has the advantage of increasing the difference between indices of refraction of adjoining layers associated with the orientation axis while the reflection of light with its plane of polarization parallel to the transverse

direction is still negligible. Differences between the transverse axis associated indices of refraction of adjoining layers after stretching should be less than 0.05 and preferably less than 0.02. Another possibility is that the selected polymer exhibits some positive birefringence due to stretching, but this can be relaxed to match the refractive index of the transverse axis of the PEN layers in a heat treatment. The temperature of this heat treatment should not be so high as to relax the birefringence in the PEN layers.

The preferred selected polymer for the polarizer of the present invention is a copolyester of the reaction product of a naphthalene dicarboxylic acid or its ester such as dimethyl naphthalate ranging from 20 mole percent to 80 mole percent and isophthalic or terephthalic acid or their esters such as dimethyl terephthalate ranging from 20 mole percent to 80 mole percent reacted with ethylene glycol. Other copolyesters within the scope of the present invention have the properties discussed above and have a refractive index associated with the transverse axis of approximately 1.59 to 1.69. Of course, the copolyester must be coextrudable with PEN. Other suitable copolyesters are based on isophthalic, azelaic, adipic, sebacic, dibenzoic, terephthalic, 2,7- naphthalene dicarboxylic, 2,6-naphthalene dicarboxylic or cyclohexanedicarboxylic acids. Other suitable variations in the copolyester include the use of ethylene glycol, propane diol, butane diol, neopentyl glycol, polyethylene glycol, tetramethylene glycol, diethylene glycol, cyclohexanedimethanol, 4-hydroxy diphenol, propane diol, bisphenol A, and 1,8-dihydroxy biphenyl, or 1,3-bis(2-hydroxyethoxy)benzene as the diol reactant. A volume average of the refractive indices of the monomers would be a good guide in preparing useful copolyesters. In addition, copolycarbonates having a glass transition temperature compatible with the glass transition temperature of PEN and with a refractive index associated with the transverse axis of approximately 1.59 to 1.69 are also useful as a selected polymer in the present invention. Formation of the copolyester or copolycarbonate by transesterification of two or more polymers in the extrusion system is another possible route to a viable selected polymer.

Referring to Fig. 26, two component orthogonal biaxial birefringent systems and the design considerations affecting the resultant optical properties will now be described. Again, the system can have many layers, but an understanding of the optical behavior of the stack is achieved by examining the optical behavior at one interface.

A biaxial birefringent system can be designed to give high reflectivity for light with

its plane of polarization parallel to one axis, for a broad range of angles of incidence, and simultaneously have low reflectivity and high transmission for light with its plane of polarization parallel to the other axis for a broad range of angles of incidence. As a result, the biaxial birefringent system acts as a polarizer, transmitting light of one polarization and reflecting light of the other polarization. By controlling the three indices of refraction of each film, nx, ny and nz, the desired polarizer behavior can be obtained. Again, the indices of refraction can be measured directly or can be indirectly observed by analysis of the spectra of the resulting film, as described herein.

Referring again to Fig. 26, the following values to the film indices are assigned for purposes of illustration: n1x = 1.88, n1y = 1.64, n1z = variable, n2x = 1.65, n2y = variable, and n2z = variable. The x direction is referred to as the extinction direction and the y direction as the transmission direction.

Equation 1 can be used to predict the angular behavior of the biaxial birefringent system for two important cases of light with a plane of incidence in either the stretch (xz plane) or the non-stretch (yz plane) directions. The polarizer is a mirror in one polarization direction and a window in the other direction. In the stretch direction, the large index differential of 1.88 - 1.65 = 0.23 in a multilayer stack with hundreds of layers will yield very high reflectivities for s-polarized light. For p-polarized light the reflectance at various angles depends on the n1z/n2z index differential.

In many applications, the ideal reflecting polarizer has high reflectance along one axis (the so-called extinction axis) and zero reflectance along the other (the so-called transmission axis), at all angles of incidence. For the transmission axis of a polarizer, it generally desirable to maximize transmission of light polarized in the direction of the transmission axis over the bandwidth of interest and also over the range of angles of interest. Average transmission at normal incidence for a narrow bandpolarizer across a 100 nm bandwidth is desirably at least 50%, preferably at least 70% and more preferably at least 90%. The average transmission at 60 degrees from the normal for p-polarized light (measured along the transmission axis) for a narrow band polarizer across a 100 nm bandwidth is desirably at least 50%, preferably at least 70% and more preferably at least 80%.

The average transmission at normal incidence for a polarizer in the transmission axis across the visible spectrum (400-700 nm for a bandwidth of 300 nm) is desirably at

least 50%, preferably at least 70%, more preferably at least 85%, and even more preferably at least 90%. The average transmission at 60 degrees from the normal (measured along the transmission axis) for a polarizer from 400-700 nm is desirably at least 50%, preferably at least 70%, more preferably at least 80%, and even more preferably at least 90%.

For certain applications, high reflectivity in the transmission axis at off-normal angles are preferred. The average reflectivity for light polarized along the transmission axis should be more than 20% at an angle of at least 20 degrees from the normal.

If some reflectivity occurs along the transmission axis, the efficiency of the polarizer at off-normal angles may be reduced. If the reflectivity along the transmission axis is different for various wavelengths, color may be introduced into the transmitted light. One way to measure the color is to determine the root mean square (RMS) value of the transmissivity at a selected angle or angles over the wavelength range of interest. The % RMS color, C_{RMS}, can be determined according to the equation:

$$C_{RMS} = \frac{\int_{\lambda 1}^{\lambda 2} ((T-\bar{T})^2)^{1/2} d\lambda}{\bar{T}}$$

where the range $\lambda 1$ to $\lambda 2$ is the wavelength range, or bandwidth, of interest, T is the transmissivity along the transmission axis, and $\bar{T}$ is the average transmissivity along the transmission axis in the wavelength range of interest.

For applications where a low color polarizer is desirable, the % RMS color should be less than 10%, preferably less than 8%, more preferably less than 3.5%, and even more preferably less than 2.1% at an angle of at least 30 degrees from the normal, preferably at least 45 degrees from the normal, and even more preferably at least 60 degrees from the normal.

Preferably, a reflective polarizer combines the desired % RMS color along the transmission axis for the particular application with the desired amount of reflectivity along the extinction axis across the bandwidth of interest. For example, for narrow band polarizers having a bandwidth of approximately 100 nm, average transmission along the

extinction axis at normal incidence is desirably less than 50%, preferably less than 30%, more preferably less than 10%, and even more preferably less than 3%. For polarizers having a bandwidth in the visible range (400-700 nm, or a bandwidth of 300 nm), average transmission along the extinction axis at normal incidence is desirably less than 40%, more desirably less than 25%, preferably less than 15%, more preferably less than 5% and even more preferably less than 3%.

Reflectivity at off-normal angles, for light with its plane of polarization parallel to the transmission axis may be caused by a large z-index mismatch, even if the in-plane y indices are matched. The resulting system thus has large reflectivity for p, and is highly transparent to s polarized light. This case was referred to above in the analysis of the mirror cases as a "p polarizer".

For uniaxially stretched polarizers, performance depends upon the relationships between the alternating layer indices for all three (x, y, and z) directions. As described herein, it is desirable to minimize the y and z index differentials for a high efficiency polarizer. Introduction of a y-index mismatch is described to compensate for a z-index mismatch. Whether intentionally added or naturally occurring, any index mismatch will introduce some reflectivity. An important factor thus is making the x-index differential larger than the y- and z-index differentials. Since reflectivity increases rapidly as a function of index differential in both the stretch and non-stretch directions, the ratios $\Delta ny/\Delta nx$ and $\Delta nz/\Delta nx$ should be minimized to obtain a polarizer having high extinction along one axis across the bandwidth of interest and also over a broad range of angles, while preserving high transmission along the orthogonal axis. Ratios of less than 0.05, 0.1 or 0.25 are acceptable. Ideally, the ratio $\Delta nz/\Delta nx$ is 0, but ratios of less than 0.25 or 0.5 also produce a useable polarizer.

Fig. 21 shows the reflectivity (plotted as -Log[1-R]) at 75° for p polarized light with its plane of incidence in the non-stretch direction, for an 800 layer stack of PEN/coPEN. The reflectivity is plotted as function of wavelength across the visible spectrum (400 - 700 nm). The relevant indices for curve a at 550 nm are $n1y = 1.64$, $n1z = 1.52$, $n2y = 1.64$ and $n2z = 1.63$. The model stack design is a linear thickness grade for quarterwave pairs, where each pair thickness is given by $dn = do + do(0.003)n$. All layers were assigned a random thickness error with a gaussian distribution and a 5% standard deviation.

Curve a shows high off-axis reflectivity across the visible spectrum along the transmission axis (the y-axis) and that different wavelengths experience different levels of reflectivity. This is due to the large z-index mismatch (• nz = 0.11). Since the spectrum is sensitive to layer thickness errors and spatial nonuniformities, such as film caliper, this gives a biaxial birefringent system with a very nonuniform and "colorful" appearance. Although a high degree of color may be desirable for certain applications, it is desirable to control the degree of off-axis color, and minimize it for those applications requiring a uniform, low color appearance, such as liquid crystal displays or other types of displays.

Off-axis reflectivity, and off-axis color can be minimized by introducing an index mismatch to the non-stretch in-plane indices (n1y and n2y) that create a Brewster condition off axis, while keeping the s-polarization reflectivity to a minimum.

Fig. 22 explores the effect of introducing a y-index mismatch in reducing off-axis reflectivity along the transmission axis of a biaxial birefringent system. With n1z = 1.52 and n2z = 1.63 (• nz = 0.11), the following conditions are plotted for p polarized light: a) n1y = n2y = 1.64; b) n1y = 1.64, n2y = 1.62; c) n1y = 1.64, n2y = 1.66. Curve a shows the reflectivity where the in-plane indices n1y and n2y are equal. Curve a has a reflectance minimum at 0°, but rises steeply after 20°. For curve b, n1y > n2y, and reflectivity increases rapidly. Curve c, where n1y < n2y, has a reflectance minimum at 38°, but rises steeply thereafter. Considerable reflection occurs as well for s polarized light for n1y • n2y, as shown by curve d. Curves a-d of Fig. 22 indicate that the sign of the y-index mismatch (n1y - n2y) should be the same as the z-index mismatch (n1z- n2z) for a Brewster minimum to exist. For the case of n1y = n2y, reflectivity for s polarized light is zero at all angles.

By reducing the z-axis index difference between layers, the off axis reflectivity can be further reduced. If n1z is equal to n2z, Fig. 17 indicates that the extinction axis will still have a high reflectivity off-angle as it does at normal incidence, and no reflection would occur along the nonstretch axis at any angle because both indices are matched (e.g., n1y = n2y and n1z = n2z).

Exact matching of the two y indices and the two z indices may not be possible in some multilayer systems. If the z-axis indices are not matched in a polarizer construction, introduction of a slight mismatch may be desired for in-plane indices n1y and n2y. This can be done by blending additional components into one or both of the material layers in

order to increase or decrease the respective y index. Blending a second resin into either the polymer that forms the highly birefringent layers or into the polymer that forms the selected polymer layers may be done to modify reflection for the transmission axis at normal and off-normal angles, or to modify the extinction of the polarizer for light polarized in the extinction axis. The second, blended resin may accomplish this by modifying the crystallinity and the index of refraction of the polymer layers after orientation.

Another example is plotted in Fig. 23, assuming n1z = 1.56 and n2z = 1.60 (• nz = 0.04), with the following y indices a) n1y = 1.64, n2y = 1.65; b) n1y = 1.64, n2y = 1.63. Curve c is for s-polarized light for either case. Curve a, where the sign of the y-index mismatch is the same as the z-index mismatch, results in the lowest off-angle reflectivity.

The computed off-axis reflectance of an 800 layer stack of films at 75° angle of incidence is plotted as curve b in Fig. 21. Comparison of curve b with curve a in Fig. 21 shows that there is far less off-axis reflectivity, and therefore lower perceived color and better uniformity, for the conditions plotted in curve b. The relevant indices for curve b at 550 nm are n1y = 1.64, n1z = 1.56, n2y = 1.65 and n2z = 1.60.

Fig. 24 shows a contour plot of equation 1 which summarizes the off axis reflectivity discussed in relation to Fig. 26 for p-polarized light. The four independent indices involved in the non-stretch direction have been reduced to two index mismatches, • nz and • ny. The plot is an average of 6 plots at various angles of incidence from 0° to 75° in 15 degree increments. The reflectivity ranges from 0.4×10^{-4} for contour a, to 4.0×10^{-4} for contour j, in constant increments of 0.4×10^{-4}. The plots indicate how high reflectivity caused by an index mismatch along one optic axis can be offset by a mismatch along the other axis.

Thus, by reducing the z-index mismatch between layers of a biaxial birefringent systems, and/or by introducing a y-index mismatch to produce a Brewster effect, off-axis reflectivity, and therefore off-axis color, are minimized along the transmission axis of a multilayer reflecting polarizer.

It should also be noted that narrow band polarizers operating over a narrow wavelength range can also be designed using the principles described herein. These can be made to produce polarizers in the red, green, blue, cyan, magenta, or yellow bands, for example.

An ideal reflecting polarizer should transmit all light of one polarization, and reflect all light of the other polarization. Unless laminated on both sides to glass or to another film with a clear optical adhesive, surface reflections at the air/reflecting polarizer interface will reduce the transmission of light of the desired polarization. Thus, it may in some cases be useful to add an antireflection (AR) coating to the reflecting polarizer. The AR coating is preferably designed to dereflect a film of index 1.64 for PEN based polarizers in air, because that is the index of all layers in the nonstretch (y) direction. The same coating will have essentially no effect on the stretch direction because the alternating index stack of the stretch direction has a very high reflection coefficient irrespective of the presence or absence of surface reflections. Any AR coating known in the art could be applied, provided that the coating does not overheat or damage the multilayer film being coated. An exemplary coating would be a quarterwave thick coating of low index material, ideally with index near the square root of 1.64 (for PEN based materials).

The number of layers in the base is selected to achieve the desired optical properties using the minimum number of layers for reasons of film thickness, flexibility, and economy. In the case of both polarizers and mirrors, the number of layers is preferably less than about 10,000, more preferably less than about 1,000.

A further criteria must be considered when designing AR constructions for non-normal incident angles with birefringent polymers such as oriented crystalline or partially crystalline polymers. In these cases, it is necessary to account for the anisotropy of the index of refraction. In other words, for non-normal angles, the reflection will depend on the index normal to the film plane as well the in-plane indices, for both the substrate and the AR construction. If the two in-plane indices are different (biaxial birefringence), these differences must be taken into account for all angles of incidence.

Figure 3 illustrates calculated reflectivities for a four layer AR construction consisting of alternating THV and PEN layers deposited on a PET substrate. The order of indices of refraction starting from the layer near the air interface is 1.37/1.74/1.37/1.74/1.65 (PET). The reflectivities are calculated for normal incidence, unpolarized light (curve a), for s-polarized light at 60E relative to the normal (curve s), and p-polarized light at 60E relative to the normal (curve p).

Figure 6 illustrates calculated transmissivities for a forty four layer AR construction consisting of alternating PEN and PMMA layers deposited on a PET

substrate. The transmissivities are calculated for normal incidence, unpolarized light.

Manufacture

AR constructions may be manufactured by co-extrusion using a feedblock method, e.g., as described in co-pending U.S. Patent Application Serial No. 08/402,041. Where the AR construction is optically coupled to a mono- or multilayer polymer base, the article is preferably formed by co-extruding the AR construction with the base to form the article in a single step.

Co-extrusion of optically thin AR layers may be difficult due to the shear forces in an extrusion system causing an unstable polymer flow. Extrusion coating of thin layers may also be difficult to control. Thus, to prepare optically thin AR layers, it is generally preferred to extrude relatively thick polymer layers and then stretch the resulting material to produce the desired final thickness. The stretching process will also result in the orientation of certain polymers, with the degree of orientation related to the amount of stretching.

The effect of shear forces produced during co-extrusion can also be reduced by co-extruding one or more relatively thick "skin layers" when forming the article. As shown in Figure 1B, article 112 is provided with a skin layer 110 that absorbs much of the shear forces developed during extrusion. In one simplified construction, skin layer 110 is placed on top of AR layer 114, and AR layer 114 is on top of base 116. By appropriate selection of the composition of the skin layer 110, the skin layer 110 can be removed from all or a portion of article 112. If the final article 112 is stretched, skin layer 110 can be removed either before or after stretching. The presence of one or more skin layers in the co-extrusion process may also assist with the production of multilayer AR stacks.

Suitable materials for the skin layer include co-extrudable polymers such as polyethylene, polypropylene, and atactic polystyrene. These materials generally will not adhere strongly to most suitable materials for the AR layer(s). The addition of the skin layer allows the AR layer(s) to be extruded without structural damage and, if desired, subsequently stretched to form optically thin layer(s).

A thick "skin layer" may be useful itself as an AR layer in reducing reflectance if it were made of a polymer having a relatively low index of refraction such as THV-500 fluoropolymer (n = 1.36). For example, in the case of a PET substrate provided with a

THV AR layer, the air/THV interface reflects only about 2.33% of the light. The THV/PET interface reflects 0.93%. Bare PET (n = 1.65) reflects 6.0%, so the use of a THV skin layer would reduce this value to 3.26%. The 0.93% reflection value at the PET/THV interface could be reduced even further by incorporating one or more intermediate layers, or by grading the index with the use of a third polymer which is miscible with both PET and
THV-500.

Another design involving skin layers is shown in Figure 2B. In this design, useful in cases where the base has only one side provided with an AR construction, two AR stacks 140 are placed roughly in the middle of an intermediate article 146. The two AR stacks are separated by an internal skin layer 142. The base 144 are oriented outward. From this construction, two articles 148, 150 can later be formed by separating skin layer 142 from the layers forming each AR stack 140. In this way, the AR stacks are not subject to high shear during the extrusion process. Additional AR stacks and/or skin layers can be extruded along the outer surfaces, if desired.

Following co-extrusion and removal of skin layers (if present), additional materials may be deposited on the outermost layer of the AR construction, in which case the stack is pre-designed using computer modeling to factor in the presence of these layers and their effect on the optical properties of the stack. For example, inorganic materials such as alumina, zirconia, silica, titania, and combinations thereof can be deposited in the form of a sol-gel. Other inorganic materials, e.g., indium-tin oxide and metals such as silver or aluminum can be vapor coated onto the outermost layer of the AR construction. If desired, the resulting construction can then be solution coated with a fluoropolymer to form a hybrid AR construction, as described above. The fluoropolymer could also be solution-coated directly onto the outermost layer of the AR construction.

<u>Applications</u>

The AR constructions are useful in a variety of applications. The particular design is selected based upon the application.

FIG. 4 shows an article 200 that may be optically coupled to a substrate to provide anti-reflective properties. It is useful in applications for which higher optical transmission and/or reduced glare are desired. Representative substrates include, e.g.,

goggles, eyeglasses, display windows, paper labels or sheets, opaque but glossy surfaces, luminares and lighting fixtures, low temperature light bulbs, computer monitors, and liquid crystal displays (both backlit and front lit).

Article 200 is also useful as a substrate for coatings such as photographic emulsions when it is desirable to suppress even the minute reflection that occurs at the solid/solid interface between the coating and substrate. Such an article may optionally be optically coupled to another article. The AR stack serves to dereflect the interface between the monolayer base film and the coating. For example, in the case of photographic emulsions designed for laser exposure, the AR stack will prevent the typical "woodgrain" pattern caused by interference of coherent light reflected from both the top and bottom interfaces of the emulsion.

Article 200 features a relatively thick, birefringent monolayer base 202, a multilayer anti-reflective stack 204 optically coupled to the base, and an additional layer 206 for providing desired mechanical, chemical, and/or electrical properties. Layer 206 may be part of the final article or it may be strippable, e.g., a strippable skin layer, that is removed to yield the final article. An optical coupling agent 208 is used to secure article 200 to a substrate. Stack 204, which includes a plurality of polymer layers 210 featuring alternating layers of birefringent polymers and low index polymers is designed to de-reflect base 202.

Article 200 is prepared by co-extruding base 202 and stack 204 in the form of a unitary article, and then stretching the article until a pre-determined thickness is reached. Stretching produces high in-plane indices of refraction in the case of crystalline and semi-crystalline polymers described above.

Base 202 is selected to provide sufficient mechanical strength and thickness for ease of handling during manufacture and application. Preferred materials include birefringent, strain-hardening materials having a glass transition temperature equal to or lower than the polymers forming stack 208. A representative polymer suitable for base 202 is polyethylene terephthalate.

It is also possible to construct article 200 without base 202. For such constructions, stack 204 should contain a sufficient number of layers such that it forms a free-standing film having a thickness, e.g., in the range of about 3-5 microns. Optical coupling agent 208 is provided directly on a surface of stack 204.

Optical coupling agent 208 may be any clear material that will wet both the substrate and article 200. Typically, the coupling agent is an optical adhesive, e.g., a pressure sensitive adhesive or epoxy resin. Preferably, the index of refraction of coupling agent 208 is intermediate that of base 202 and the substrate.

Suitable materials for layer 206 include coatings to lower the surface energy and/or coefficient of friction of the article to aid in cleaning the article or preventing surface abrasions, and antistatic or electromagnetic interference coatings. Layer 206 may also be in the form of a protective skin layer that is either strippable or permanent (in which case it becomes part of the final article). For example, where article 200 is designed to reduce the reflectance at solid/solid interfaces such as the interface between a base film and a coating, layer 206 may take the form of a permanent skin layer having an index of refraction matched to that of the coating. Layer 206 may be applied after co-extrusion, but either prior to, or after, stretching. In addition, multiple layers may be used. In all cases where layer 206 is designed to become part of the final article, the thickness and index of refraction of layer 206 must be included as part of the AR stack optical design.

Article 200 may optionally include a functional coating or film (not shown) in between base 202 and coupling agent 208. Because it is placed on the back side of base 202, it does not affect the design or function of AR stack 204 located on the opposite side of base 202. Article 146, shown in Fig. 2B, may similarly include such a coating on the back side of base 144. Examples of suitable coatings include transparent conducting films for EMI shielding or IR rejection, anti-static films, UV protective coatings, colored or neutral grey coatings that control light transmission, and polarizing coatings.

The article shown in FIG. 2A may be used without laminating it to a substrate. It is useful in applications where high transparency is desired. Examples include protective face masks, goggles, window coverings that include a thermally insulating air gap, insulation layers inside multi-pane glass windows, overhead projection transparencies and associated covers, and high transparency wrapping material for packaging.

It is possible to eliminate base 134, in which case stacks 132 are provided in the form of a single, free-standing film. One or more layers for providing desired mechanical, chemical, and/or electrical properties may be included as well. For example, in the case of face masks and goggles, it may be desirable to include a hydrophilic coating to prevent fogging.

FIG. 5 shows an article 300 which may be optically coupled to a substrate to provide anti-reflective properties, or used by itself. It is particularly useful in applications where high color saturation and low glare are desired. Examples of such applications include edge filters with high transmission and sharp spectral cut-offs (including hot and cold mirrors), reflective color filters with high color purity in both reflection and transmission (e.g., for use as label stock, security/verification laminates, color filters for projection displays, visible colored window decorations, infrared reflecting window film, colored adhesive-backed tapes, colored gift wrap, colored packaging film, color films for advertising and the like, etc.), multilayer polymeric polarizers, and multilayer tear-resistant films having low glare.

As shown in FIG. 5, article 300 features a multilayer base 302 surrounded on each side with a multilayer anti-reflective stack 304. Each stack 304, in turn is provided with a skin layer 306, followed by another multilayer anti-reflective stack 308. Examples of the former include multilayer polymeric polarizers and mirrors. To protect outer anti-reflective stacks 308 during extrusion, article 300 may further be provided with strippable skin layers (not shown). Where article 300 is designed for application to a separate substrate, one of anti-reflective stacks 308 may be eliminated and replaced with an optical coupling agent (not shown) for coupling article 300 to the substrate.

Multilayer base 302 may be an article with utility on its own that gains functionality by addition of anti-reflective stacks, or it may be a base film that is added to an anti-reflective stack to give the anti-reflective stack additional mechanical strength or stiffness.

Anti-reflective stacks 304 are particularly useful in the case of multilayer optical film bases such as polarizers and mirrors. Preferably, anti-reflective stacks 304 are designed to suppress side band ripples and thereby aid in providing a uniformly low reflectivity at wavelengths outside of a high reflectivity bandstop, or on the low reflectivity side of an edge filter. Skin layers 306 (which effectively decouple the interference effects of anti-reflective stacks 308 and anti-reflective stacks 304) also help suppress the asymptotic sideband ripple from a stopband, as they are equivalent to immersing multi-layer stack 302 in a higher index medium. Anti-reflective stacks 308 further operate to eliminate the air/skin interface which is a source of reflection from the article.

Other embodiments are within the following claims.

What is claimed is:

1. An article comprising a plurality of polymer layers,

each of said polymer layers having a thickness no greater than about 1 micrometer and collectively forming a free-standing film,

said polymer layers being selected such that when said article is optically coupled to a surface of a substrate having a refractive index of about 1.50, said article reduces the reflectivity of said substrate at said surface over a wavelength range of interest by a factor of at least about 2 at normal angles of incidence.

2. An article according to claim 1 wherein said layers are selected from the group consisting of polymer compositions that are co-extrudable with each other.

3. An article according to claim 1 wherein said article comprises two adjoining polymer layers in which the refractive indices of said adjoining layers are different from each other.

4. An article according to claim 1 comprising a low index polymer layer having an index of refraction less than about 1.55.

5. An article according to claim 1 comprising a low index polymer layer selected from the group consisting of silicone polymers, fluoropolymers, fluoro-chloropolymers, methacrylate polymers, polyester copolymers, and combinations thereof.

6. An article according to claim 1 comprising a low index polymer layer comprising a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene terpolymer.

7. An article according to claim 1 comprising a high index polymer layer selected from the group consisting of polyesters, polycarbonates, polysulfones, polyethersulfones, and combinations thereof.

8. An article comprising a plurality of polymer layers,

each of said polymer layers having a thickness no greater than about 1

micrometer and collectively forming a free-standing film,

said polymer layers being selected such that the reflectivity measured in air over a wavelength range of interest at normal angles of incidence is no greater than about 6%.

9. An article in the form of a free-standing film comprising:

(a) a base comprising a polymer layer having a major surface; and

(b) an anti-reflective stack optically coupled to said major surface of said base that reduces the reflectivity of said base at said major surface over a first wavelength range of interest,

said stack comprising alternating layers of (i) high index polymers having an index of refraction greater than about 1.55 and (ii) low index polymers having an index of refraction less than about 1.55.

10. A process for preparing an article comprising co-extruding a plurality of polymer compositions with each other to form a plurality of polymer layers in the form of a free-standing film,

said layers being selected such that when said article is optically coupled to a substrate, said article reduces the reflectivity of said substrate over a wavelength range of interest.

11. A process for preparing an article comprising:

(a) co-extruding a plurality of polymer compositions with each other to form a free-standing film,

said film comprising:

(i) a base comprising a polymer layer having a major surface;

(ii) a precursor anti-reflective construction comprising a polymer layer; and

(iii) at least one removable polymer layer; and

(b) stretching said film to convert said precursor anti-reflective construction to an anti-reflective construction optically coupled to said major surface of said base and selected to reduce the reflectivity of said base at said major surface over a wavelength range of interest.

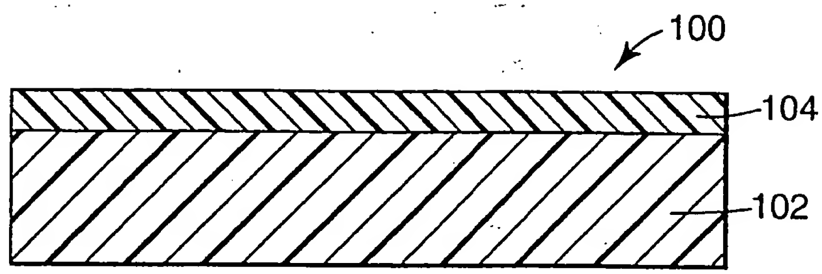


Fig. 1A

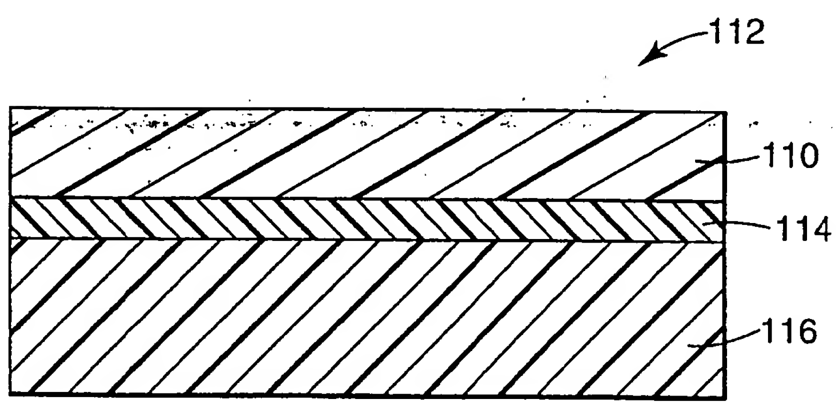


Fig. 1B

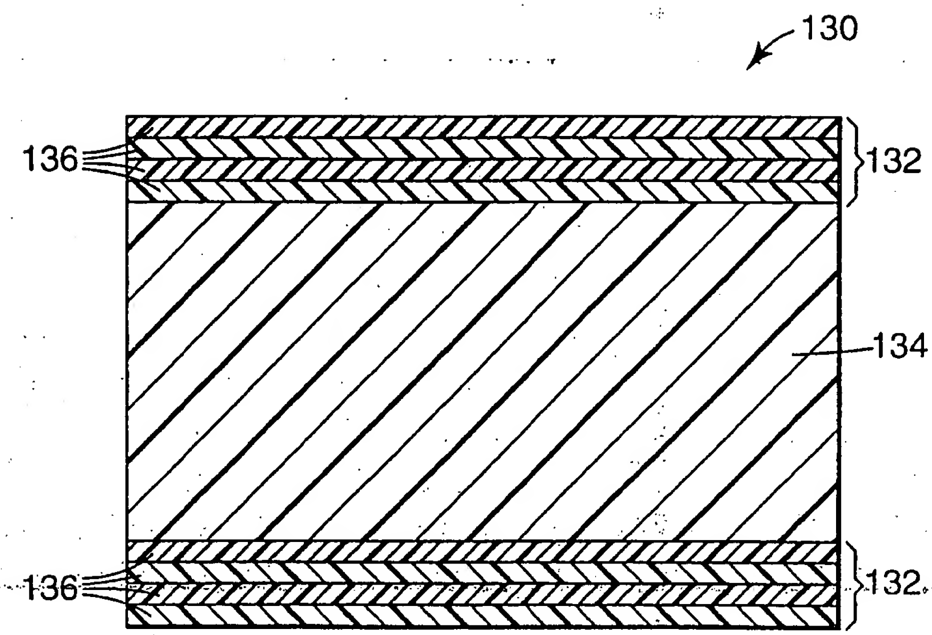


Fig. 2A

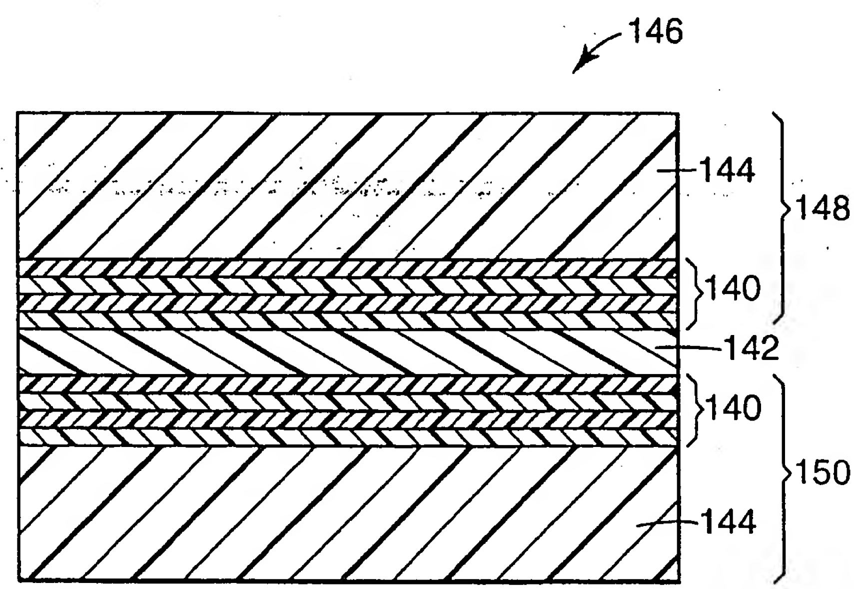


Fig. 2B

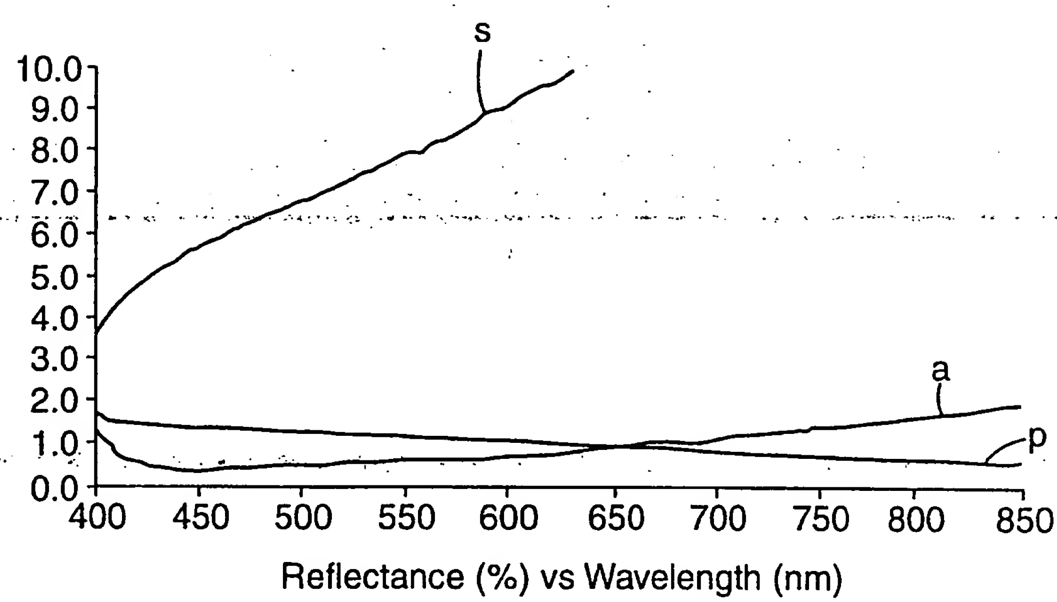

s
a
p
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
400
450
500
550
600
650
700
750
800
850
Reflectance (%) vs Wavelength (nm)

Fig. 3

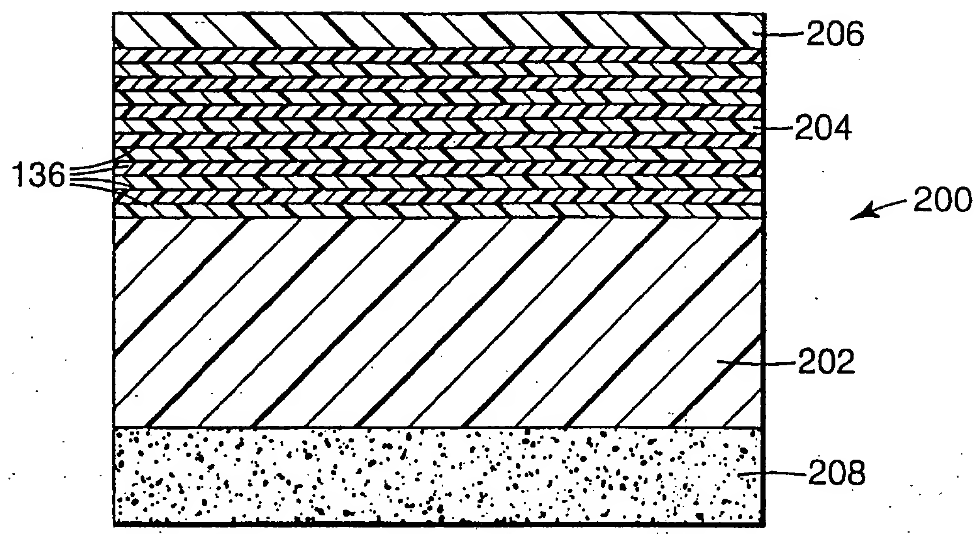


Fig. 4

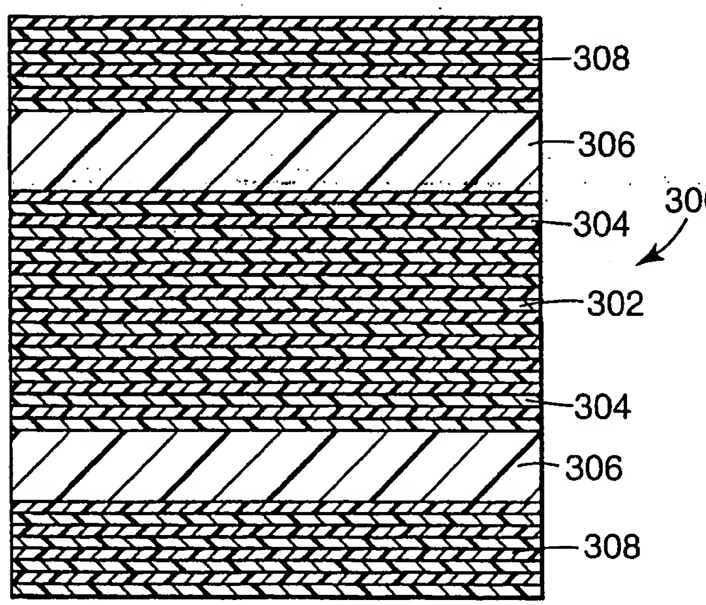


Fig. 5

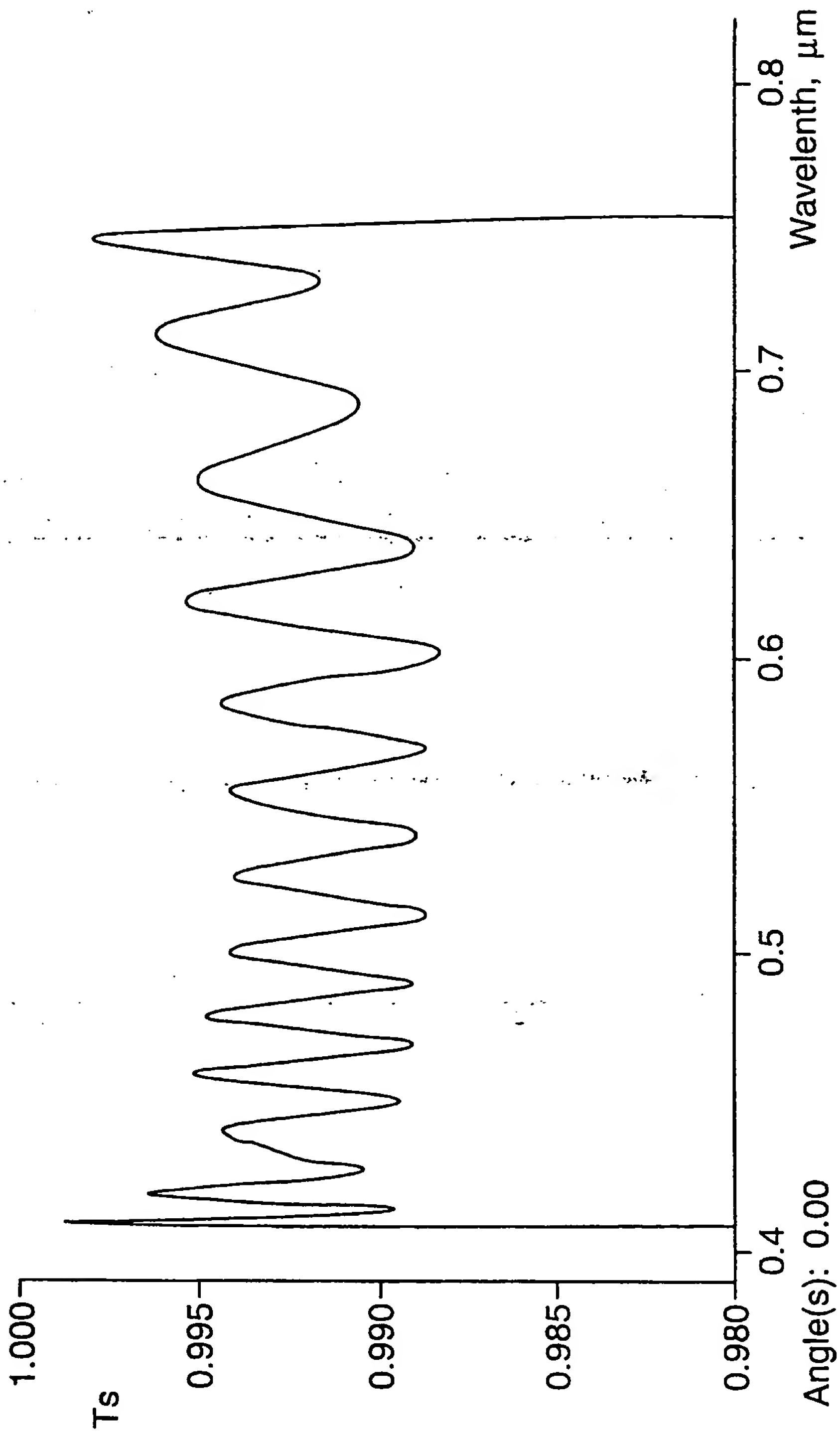

Ts
1.000
0.995
0.990
0.985
0.980
Angle(s): 0.00
0.4
0.5
0.6
0.7
0.8
Wavelenth, µm

Fig. 6

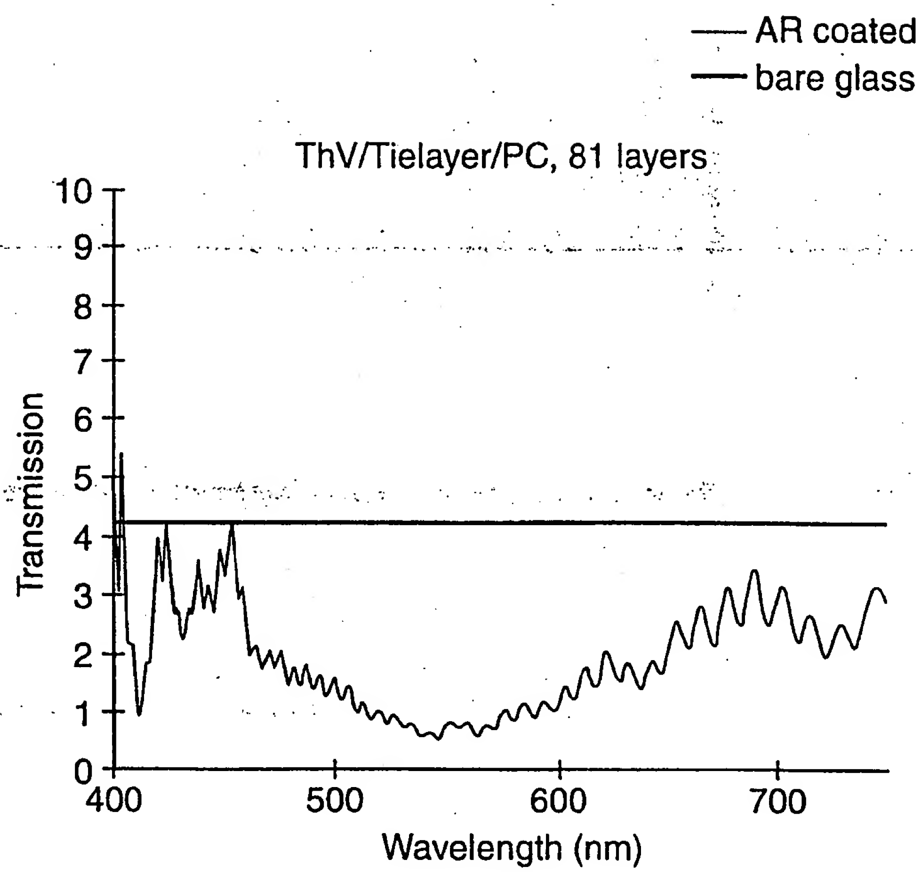
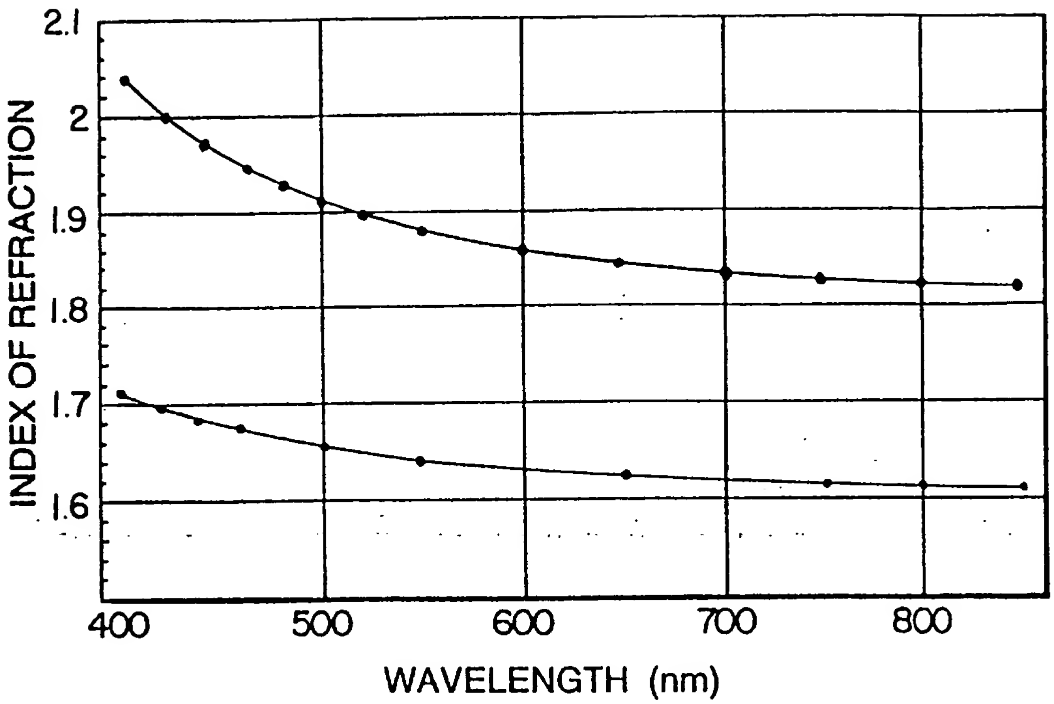

AR coated
bare glass
ThV/Tielayer/PC, 81 layers
Transmission
0
1
2
3
4
5
6
7
8
9
10
400
500
600
700
Wavelength (nm)

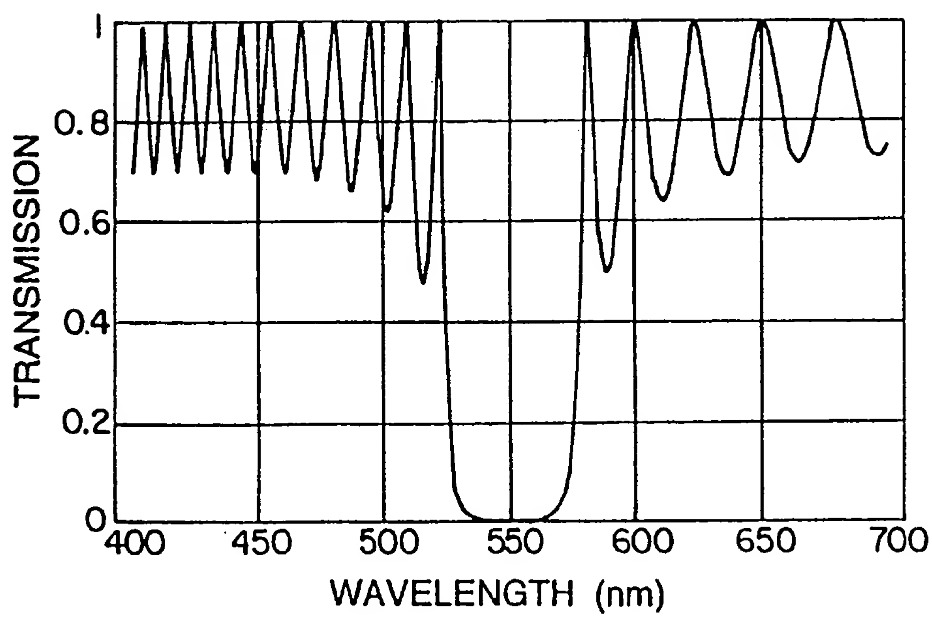
Fig. 7

Fig. 8



2.1
2
1.9
1.8
1.7
1.6
INDEX OF REFRACTION
400
500
600
700
800
WAVELENGTH (nm)

Fig. 9



1
0.8
0.6
0.4
0.2
0
TRANSMISSION
400
450
500
550
600
650
700
WAVELENGTH (nm)

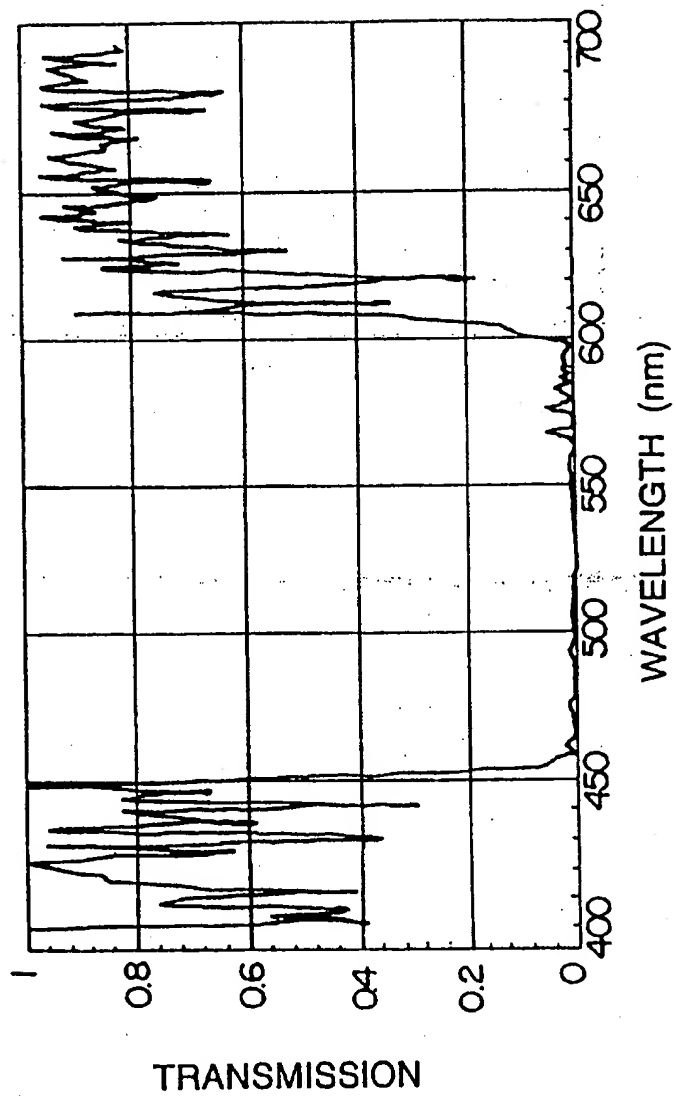

TRANSMISSION
1
0.8
0.6
0.4
0.2
0
WAVELENGTH (nm)
400
450
500
550
600
650
700

Fig. 10

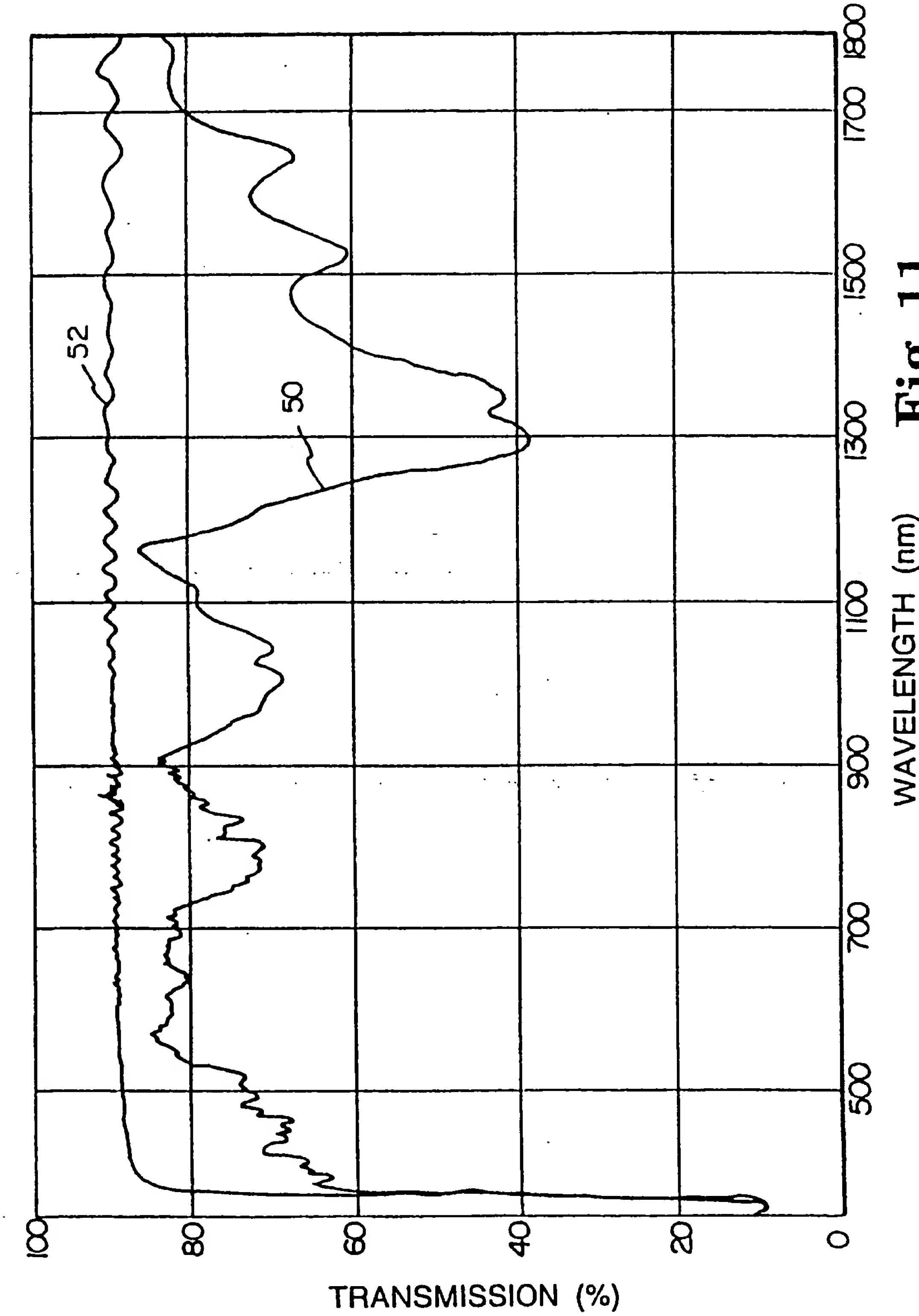

52
50
100
80
60
40
20
0
TRANSMISSION (%)
500
700
900
1100
1300
1500
1700
1800
WAVELENGTH (nm)

Fig. 11

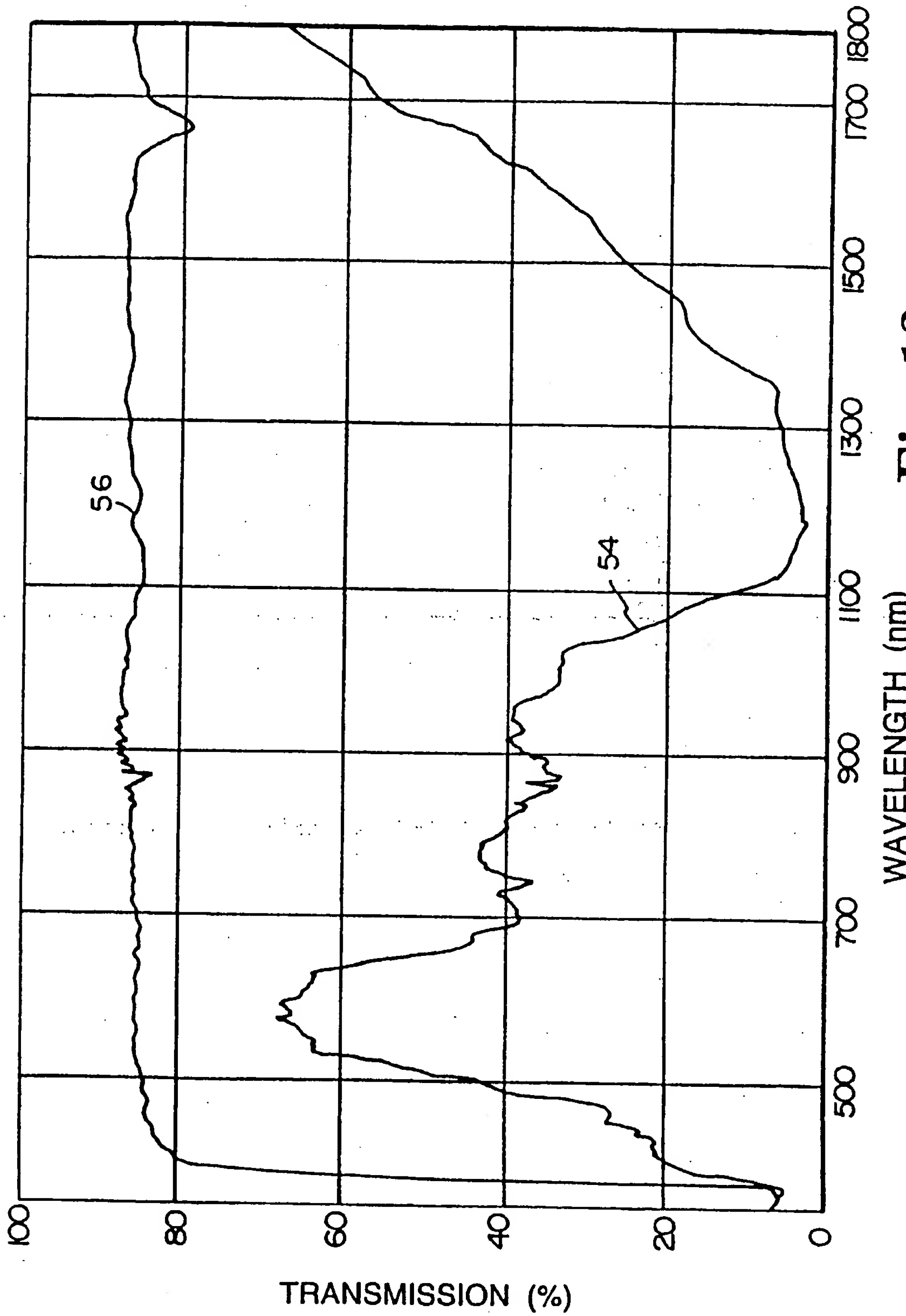

100
80
60
40
20
0
TRANSMISSION (%)
500
700
900
1100
1300
1500
1700
1800
WAVELENGTH (nm)
56
54

Fig. 12

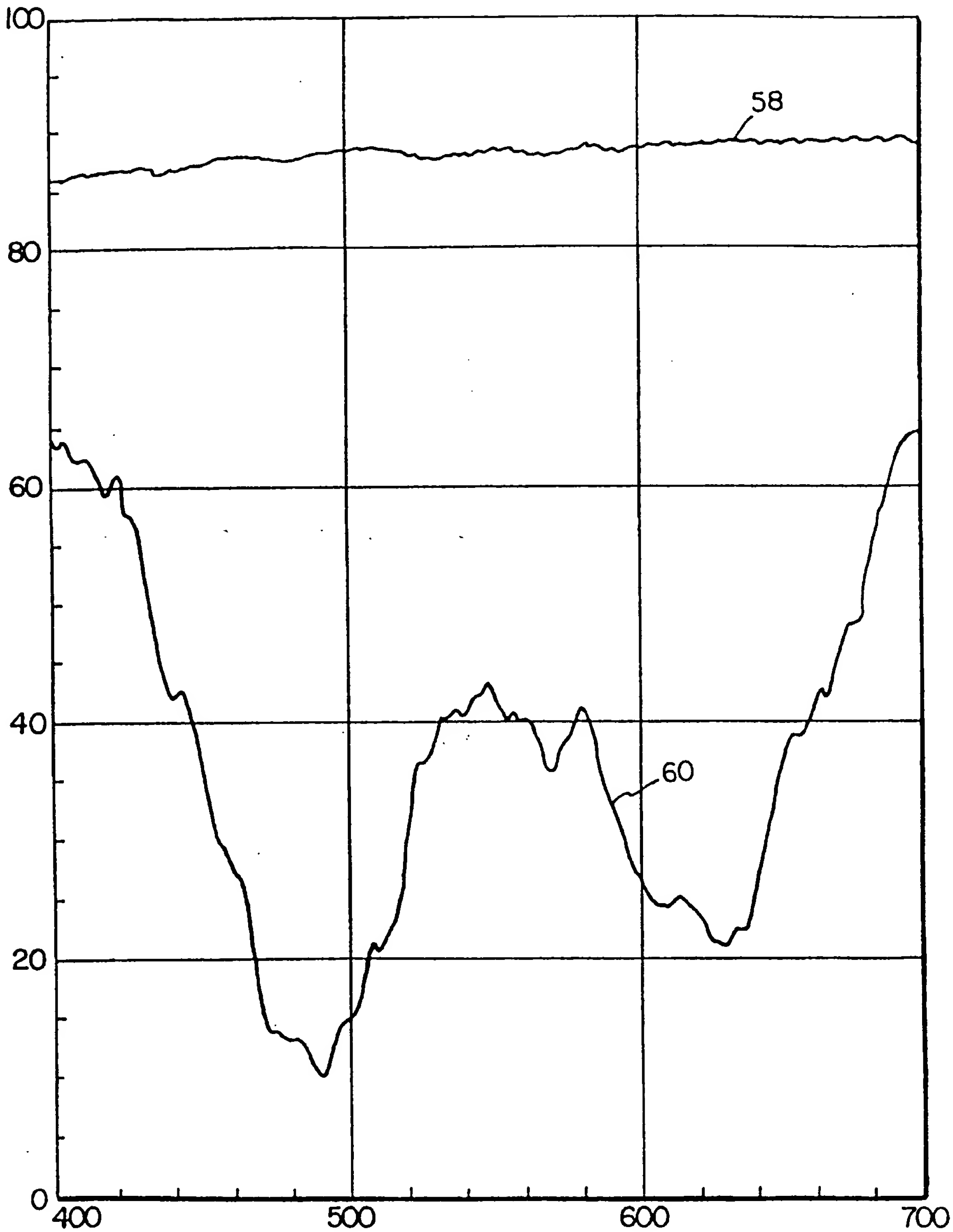


Fig. 13

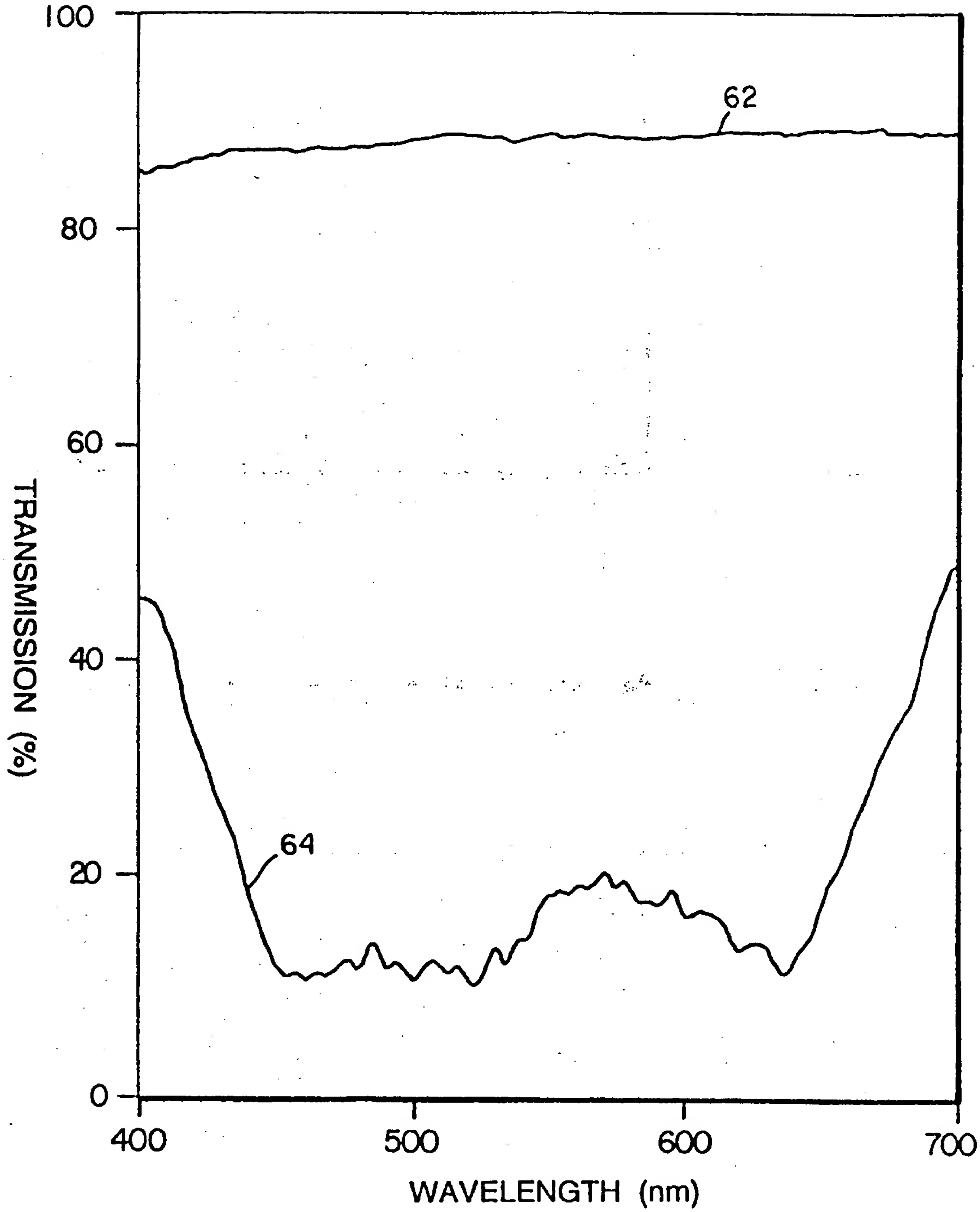

100
80
60
40
20
0
TRANSMISSION (%)
62
64
400
500
600
700
WAVELENGTH (nm)

Fig. 14

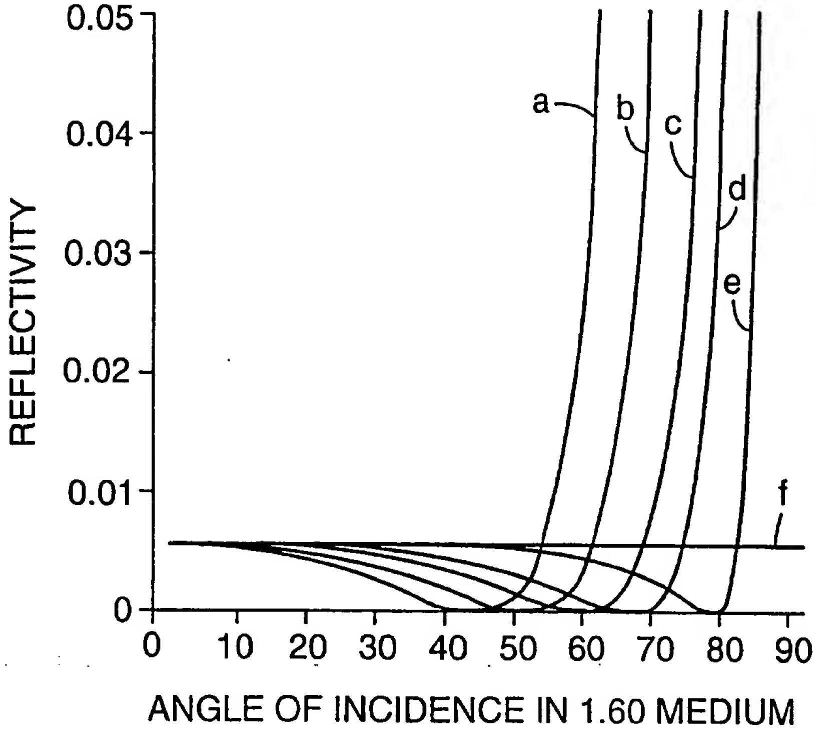

0.05
0.04
0.03
0.02
0.01
0
REFLECTIVITY
a
b
c
d
e
f
0
10
20
30
40
50
60
70
80
90
ANGLE OF INCIDENCE IN 1.60 MEDIUM

Fig. 15

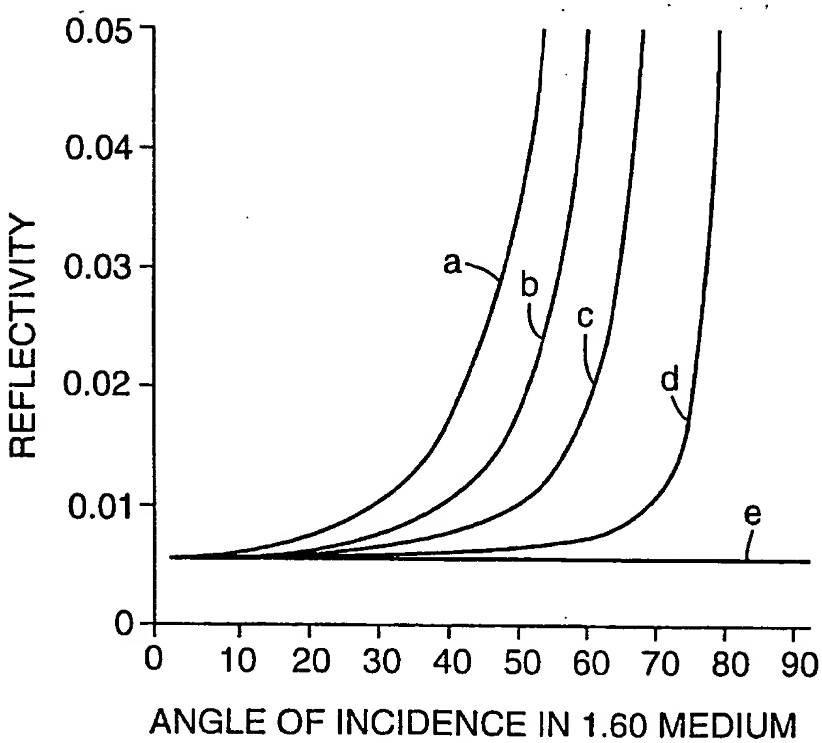

0.05
0.04
0.03
0.02
0.01
0
REFLECTIVITY
a
b
c
d
e
0
10
20
30
40
50
60
70
80
90
ANGLE OF INCIDENCE IN 1.60 MEDIUM

Fig. 16

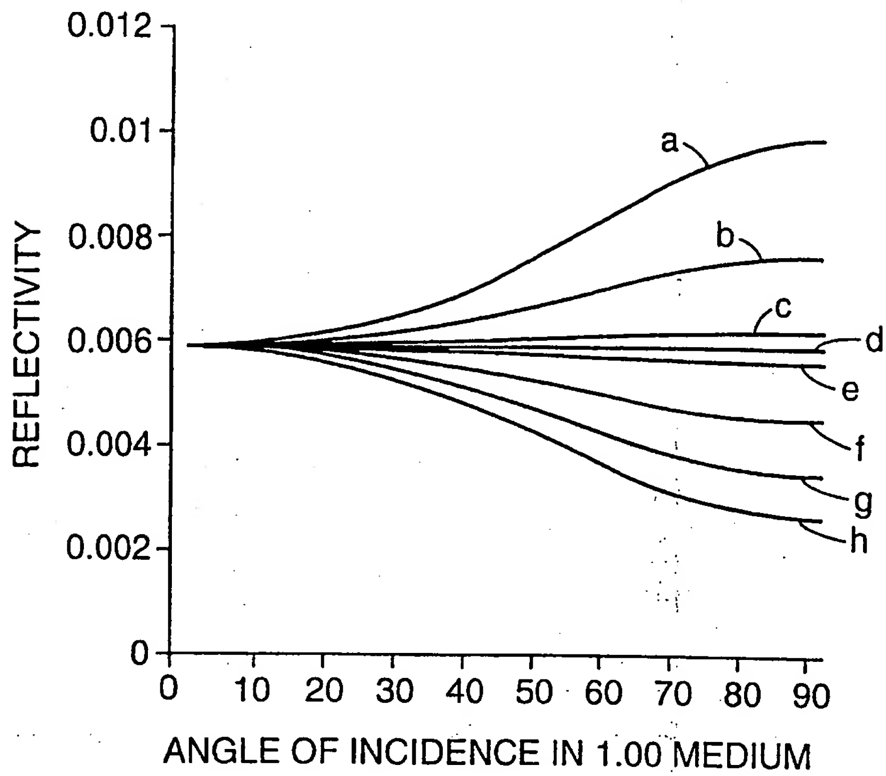

0.012
0.01
0.008
0.006
0.004
0.002
0
REFLECTIVITY
a
b
c
d
e
f
g
h
0
10
20
30
40
50
60
70
80
90
ANGLE OF INCIDENCE IN 1.00 MEDIUM

Fig. 17

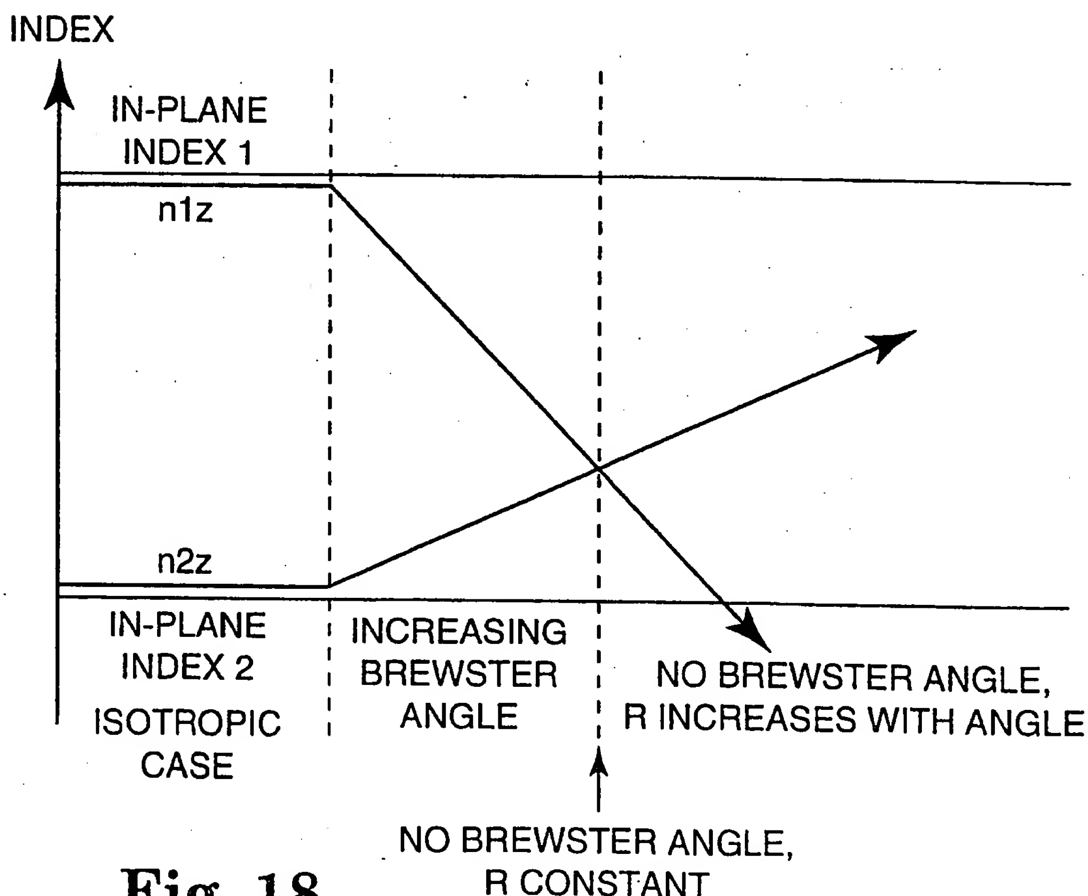

INDEX
IN-PLANE INDEX 1
n1z
n2z
IN-PLANE INDEX 2
ISOTROPIC CASE
INCREASING BREWSTER ANGLE
NO BREWSTER ANGLE, R INCREASES WITH ANGLE
NO BREWSTER ANGLE, R CONSTANT

Fig. 18

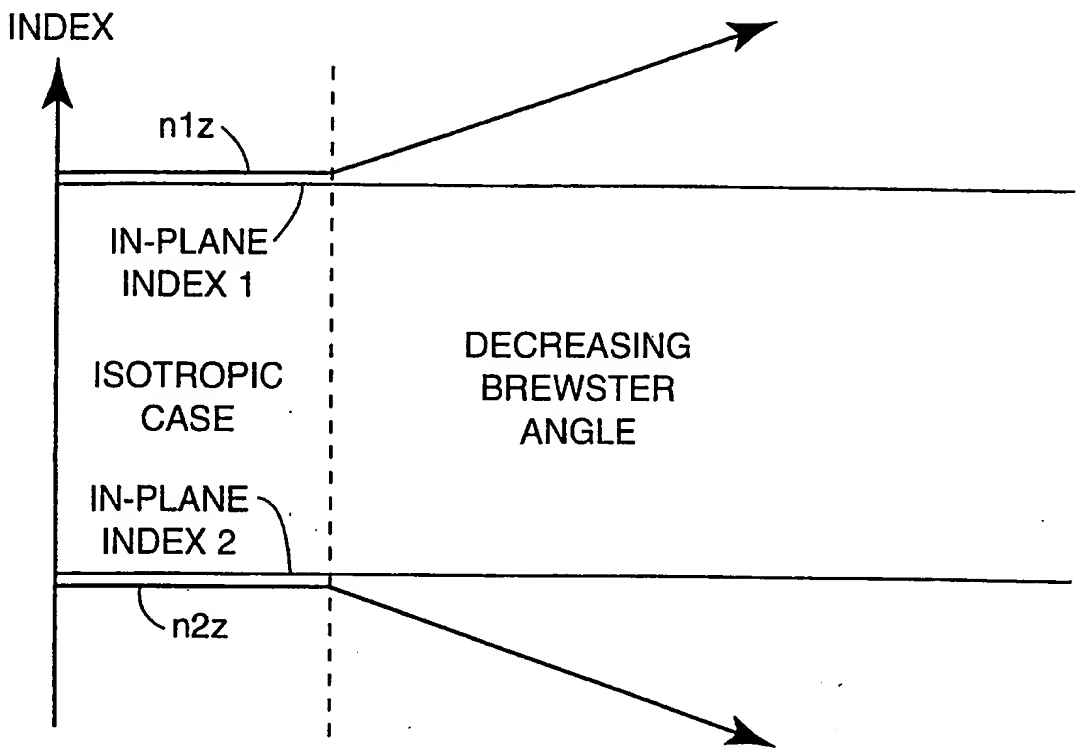

INDEX
n1z
IN-PLANE
INDEX 1
ISOTROPIC
CASE
DECREASING
BREWSTER
ANGLE
IN-PLANE
INDEX 2
n2z

Fig. 19

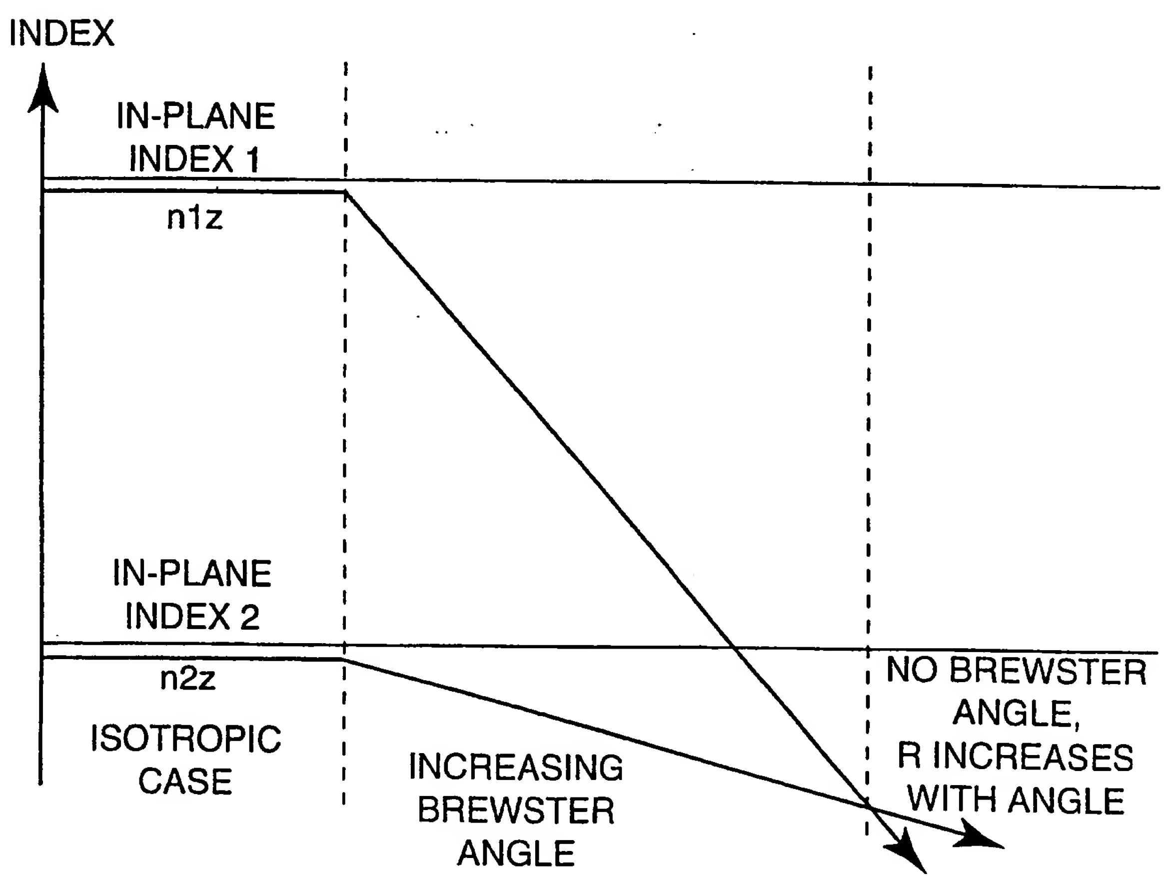

INDEX
IN-PLANE
INDEX 1
n1z
IN-PLANE
INDEX 2
n2z
ISOTROPIC
CASE
INCREASING
BREWSTER
ANGLE
NO BREWSTER
ANGLE,
R INCREASES
WITH ANGLE

Fig. 20

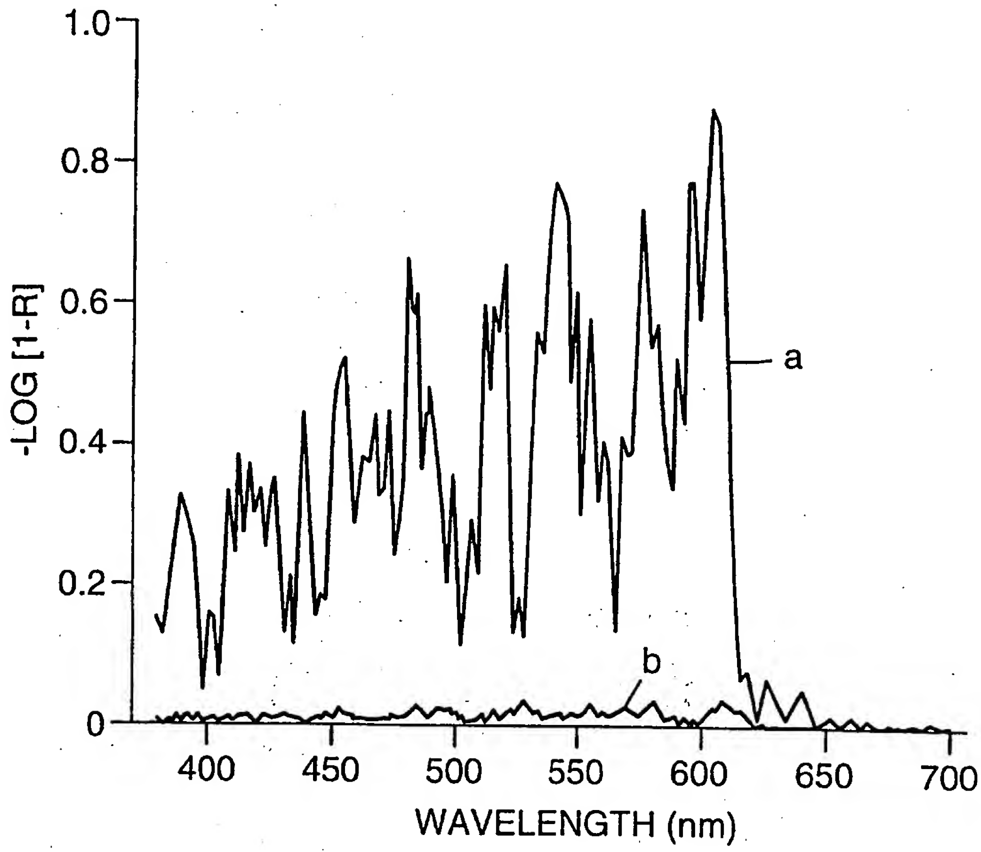

1.0
0.8
0.6
0.4
0.2
0
-LOG [1-R]
400
450
500
550
600
650
700
WAVELENGTH (nm)
a
b

Fig. 21

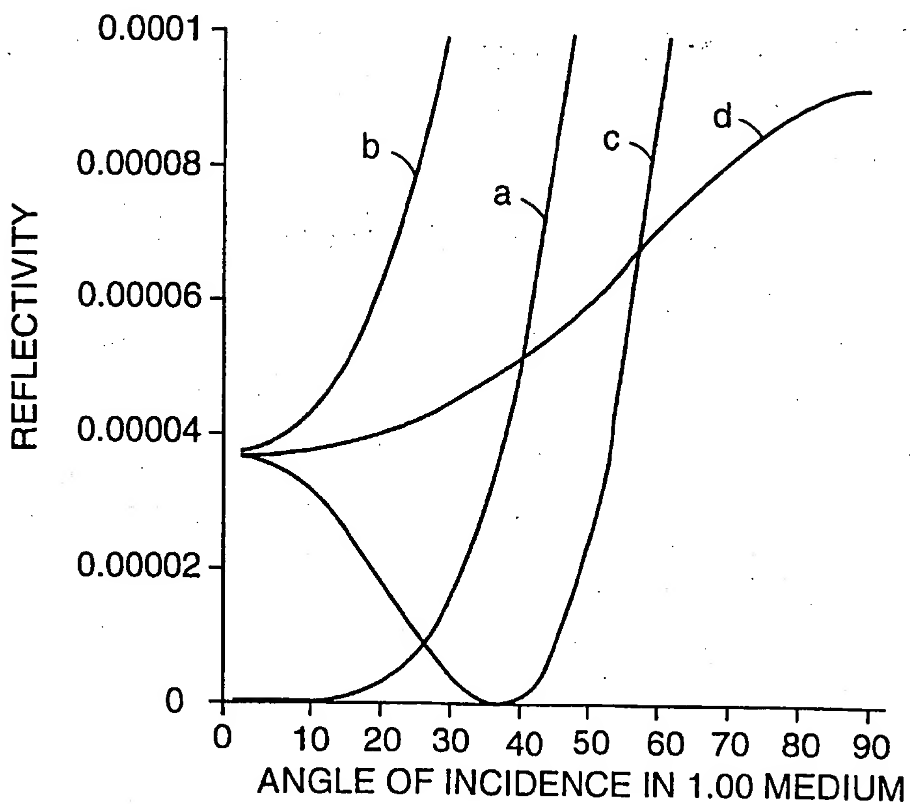

0.0001
0.00008
0.00006
0.00004
0.00002
0
REFLECTIVITY
0
10
20
30
40
50
60
70
80
90
ANGLE OF INCIDENCE IN 1.00 MEDIUM
a
b
c
d

Fig. 22

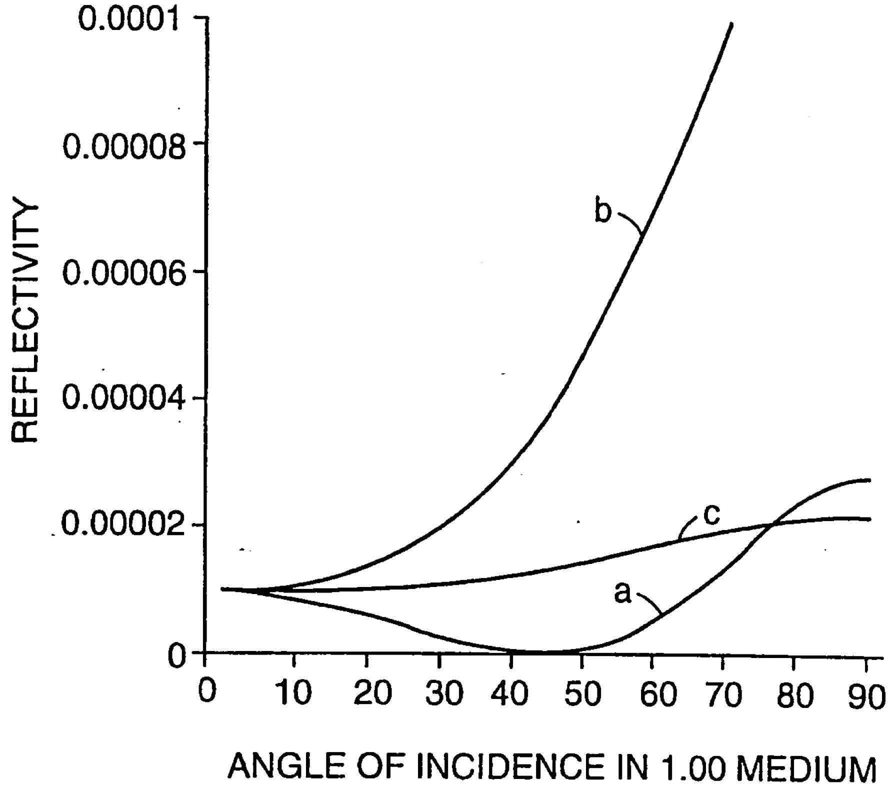

0.0001
0.00008
0.00006
0.00004
0.00002
0
REFLECTIVITY
b
c
a
0
10
20
30
40
50
60
70
80
90
ANGLE OF INCIDENCE IN 1.00 MEDIUM

Fig. 23

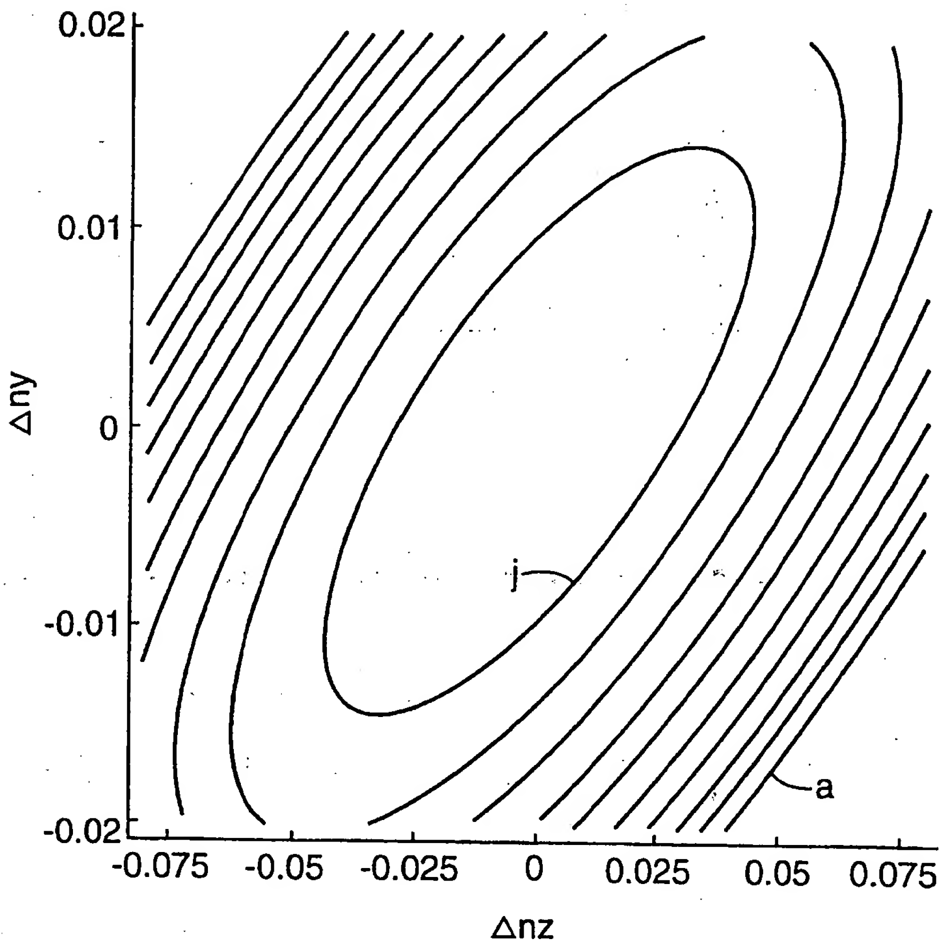


Fig. 24

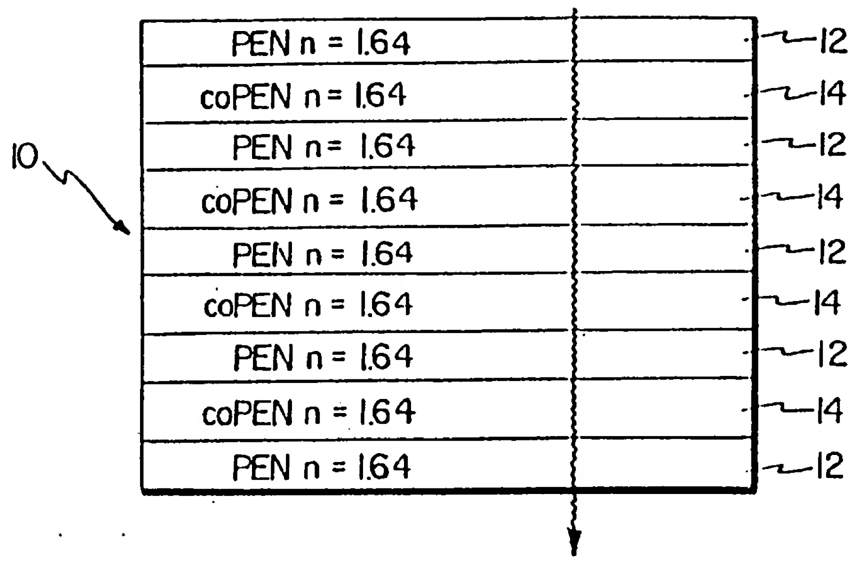


Fig. 25a

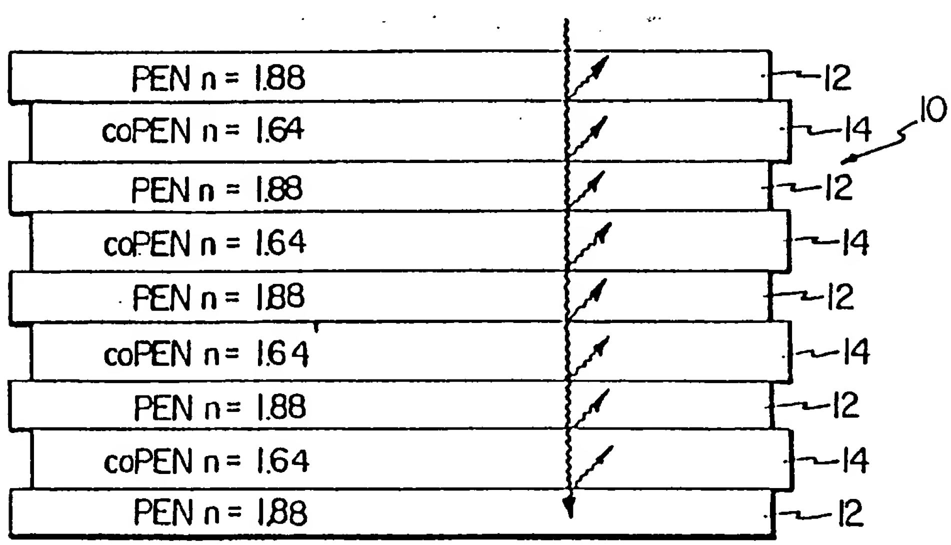


Fig. 25b

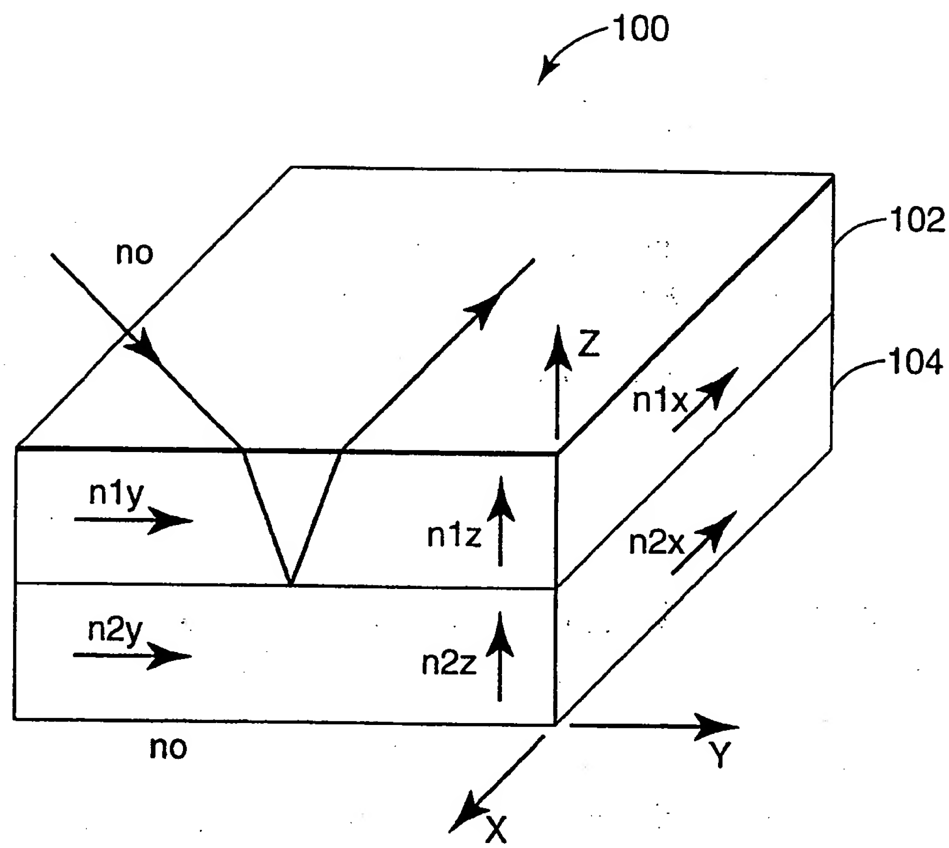


Fig. 26

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00712

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B1/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 564 134 A (CANON KK) 6 October 1993	1,3-5, 7-9
A	see page 3, line 3 - line 53 see figures 1,2,6 ---	10,11
X	WO 97 48992 A (YAZAKI CORP ;CHEN DIN GUO (US); YAN YONGAN (US); RAYCHAUDHURI SATY) 24 December 1997	1,3,4, 7-9
A	see page 2, line 5 - page 3, line 29; figures 1,2 ---	10,11
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 127 (P-201), 3 June 1983 & JP 58 046301 A (TORAY KK), 17 March 1983 see abstract --- -/--	1,3,4,7, 9

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 May 1999	14/05/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hervé, D

1

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 99/00712

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 01788 A (MINNESOTA MINING & MFG) 16 January 1997 see examples 2-4 -----	10,11

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/00712

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0564134	A	06-10-1993	JP	6018705	A	28-01-1994
			US	5392156	A	21-02-1995
WO 9748992	A	24-12-1997	US	5856018	A	05-01-1999
			AU	3479297	A	07-01-1998
			EP	0907899	A	14-04-1999
			JP	10058580	A	03-03-1998
WO 9701788	A	16-01-1997	AU	5804296	A	30-01-1997
			EP	0871923	A	21-10-1998